Photolysis of polychlorinated biphenyls by solid-phase microextraction
''On-fibre'' versus aqueous photodegradation

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Abstract

The photodegradation kinetics of polychlorinated biphenyls ''on-fibre'' is described. The utilisation of solid-phase microextraction (SPME) fibres to monitor photolysis pathways and determine photoproducts constitutes a new approach that exploits the solvent-free aspect and concentration possibilities of this technique. Direct photolysis of aqueous solutions containing polychlorinated biphenyls (PCBs) was also undertaken and SPME was used in this case for photoproduct extraction purposes. Reductive dechlorination was the main decomposition mechanism in both procedures. Less-chlorinated biphenyls are the principal photoproducts and, among these, some toxic coplanar species have been detected. The influence of irradiation time was evaluated for both treatments. SPME was found to be a good choice for the extraction of photoproducts in experiments conducted in the classical way (extraction after photolysis). Moreover, it is demonstrated that photolysis of PCBs ''on fibre'' is realistic and provides the possibility of evaluating the phototransformation of these pollutants at environmental levels. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photolysis; Photodegradation; Solid-phase microextraction; Polychlorinated biphenyls

1. Introduction

There is analytical interest in determining the presence of polychlorinated biphenyls (PCBs) in the environment, because their degradation mechanisms after disposal or dissemination are complex and they tend to bioaccumulate. Only intentional destruction processes, such as incineration and chemical degradation (e.g. dechlorination with metallic sodium), can reduce their levels [1]. However, incineration, unless very carefully controlled, can lead to their partial oxidation to the even more toxic polychlorinated benzofurans and dioxins [2].

PCBs are very lipophilic compounds that can easily be removed from aqueous solution and concentrated on a hydrophobic support such as alkylsilylated silica gel, where it is possible to photolyze them by external irradiation. Since the reaction conditions affect reactivity and product distribution, photodegradation of PCBs bound to hydrophobic surfaces is of much interest [3]. Some solid-phase microextraction (SPME) fibres are a suitable alternative to conduct this type of study, providing us with the advantage of preconcentration and thus allowing us to work with dilute solutions that better imitate environmental levels. This leads us to the first aspect of the research described in this

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paper: ''on-fibre'' photodegradation studies of poly-chlorinated biphenyls, which demonstrates a new analytical approach where the SPME fibre acts as a solid support [4]. Current and potential applications of this new technique are described.

Because all chlorobiphenyls are poorly soluble in water, early work on PCB photochemistry was carried out in alkanes and alcohols, but these solvents, especially the alkanes, are poor mimics of water, the environmental liquid. However, some work was also performed on aqueous photochemistry [5], but mainly using photocatalysis to complete the mineralization of PCBs [5–8].

The overall photochemistry in both organic and aqueous media is predominantly dechlorination [9], but, depending on the solvent used, some solvent derivatives can also be found [5,10–13]. Nevertheless, no PCB–solvent adducts are found in alkaline 2-propanol [14], in isooctane [15] or in hexane [11,16]. Moreover, when photocatalytic degradation is performed, other, more-polar intermediates can appear [7]. Photochemical decomposition using alkaline isopropyl alcohol would not be useful in aqueous media because water inhibits the reaction by protonating the reactive radical [17]. Taking these considerations into account, the comparatively few studies performed in plain water, and the use of photocatalysts or higher levels of PCBs than those present in the aquatic environment, lead us to the second aspect of this research: the investigation of aqueous photochemistry with environmental concentrations of PCBs, exploiting the preconcentration power of SPME to follow the photodegradation pathway and to evaluate the photoproducts generated.

It has been demonstrated that SPME is a suitable technique for the determination of contaminants in water samples and other matrices [18], offering important advantages for the extraction and concentration of several pollutants, including PCBs [19]. This is not the first time that SPME has been applied to the extraction and/or identification of photoproducts [20,21] or biodegradation products [22], but our research group is the first to use SPME fibre as the photoreaction support [4]. When photolysis takes place directly on the fibre, all photoproducts, with the exception of those exceptionally volatile, remain in it, so the whole system (primary compounds and photoproducts) can be analysed simultaneously. This would provide excellent information regarding the environmental behaviour of the compounds, suggesting photolysis mechanisms and photodegradation pathways.

The aim of this study was to use this new approach of the SPME technique as a support for direct extraction and photoreaction studies of environmentally relevant compounds. On the other hand, it is demonstrated that SPME is a good choice for the extraction of photoproducts in experiments conducted in the classical way (extraction after photolysis), by applying this scheme to the study of PCB photodegradation in water. The reaction pathways and photoproducts identified in ''on-fibre'' as well as in direct photolysis are discussed and comparative studies are presented.

2. Experimental

2.1. Reagents

The mixture of 10 PCBs used in this study covers a range of congeners from three to seven chlorine substituents and was prepared with: 2,4,4′-trichlorobiphenyl (PCB 28), 2,4′,5-trichlorobiphenyl (PCB 31), 2,2′,5,5′-tetrachlorobiphenyl (PCB 52), 2,2′,4,5,5′-pentachlorobiphenyl (PCB 101), 2,3,3′,4,4′-pentachlorobiphenyl (PCB 105), 2,3′,4,4′,5-pentachlorobiphenyl (PCB 118), 2,2′,3,4,4′,5′-hexachlorobiphenyl (PCB 138), 2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB 153), 2,3,3′,4,4′,5-hexachlorobiphenyl (PCB 156) and 2,2′,3,4,4′,5,5′-heptachlorobiphenyl (PCB 180), all supplied by Ultra Scientific (North Kingston, RI, USA).

The solvent for the stock solutions was isooctane. Water solutions were prepared by the addition of a PCB intermediate acetone standard solution of the 10 model compounds. The corresponding concentrations of each congener in the working solutions were in the 10–100 ng/L range for ''on-fibre'' photodegradation experiments and in the 200–1200 ng/L range for aqueous photolysis experiments (Table 1).

All the remaining solvents and reagents used were purchased from Merck (Mollet del Vallés, Barcelona, Spain).

Table 1
Concentrations in working solutions and representative ions for each individual PCB congener

PCB	Concentration (ng/L)		Precursor ion (m/z)	Representative ions	
	"On-fibre" experiments	Aqueous experiments		(MS)	(MS–MS)
28+31	86.5	1152	258	256+258	186+188
52	21.7	288.8	292	290+292	220+222
101	28.2	376	325.4	326+328	254+256
118	37.2	495.2	325.4	326+328	254+256
153	57.3	763.2	359.8	360+362	288+290
105	67.4	897.2	325.4	326+328	254+256
138	71.05	946.4	359.8	360+362	288+290
156	82.6	1100	359.8	360+362	288+290
180	71.5	952	395.8	394+396	324+326

The numbering system for PCBs suggested by IUPAC was used throughout this study [23].

2.2. Solid-phase microextraction and photodegradation procedures

Headspace (HS) SPME sampling of PCBs in aqueous matrices was adapted from the procedure described by Llompart et al. [19]. Fifteen milliliters of a water sample were placed in 22 mL vials, and heated for 10 min at the extraction temperature of 100 °C. The fibre (100 μm, polydimethylsiloxane, Supelco) was then exposed to the headspace above the sample for 30 min and thermally desorbed in the GC injection port for 2 min. The fibre was cleaned at 270 °C for 3 min between extractions to avoid carryover.

A new laboratory photoreactor model based on previous prototypes [24,25] was used for photolysis experiments: two low-pressure mercury lamps (8–10 W) were combined in an arrangement that allows easy positioning of the object to be irradiated. For "on-fibre" photolysis experiments, after HS-SPME extraction the SPME fibre, with the analytes already adsorbed, was subjected to 254 nm irradiation for the desired time in an efficient hood for adequate safety. For aqueous photolysis experiments, two 3 mL aliquots of an aqueous solution containing the 10-PCB mixture were placed in synthetic quartz precision cells and submitted to UV radiation as described above. After the designed irradiation time (from 2 to 90 min) the 6 mL photolyzed solution was placed in 22 mL headspace vials and subjected to the same

SPME procedure. In this study, other SPME fibres were tested: 65 μm polydimethylsiloxane–divinylbenzene (PDMS–DVB) and 75 μm Carboxen–polydimethylsiloxane (Carboxen–DVB) (Supelco).

For each set of experiments a control extraction (same SPME procedure but without irradiation) was carried out. In addition, all experiments were conducted in duplicate.

2.3. Chromatographic conditions

Analyses were performed on a Varian 3800 gas chromatograph (Varian, Walnut Creek, CA, USA) equipped with a 1079 split/splitless injector and a Saturn 2000 ion trap spectrometer (Varian) with a module for MS–MS analysis. The GC–MS–MS system was operated by Saturn GC–MS workstation v 5.4 software. The MS–MS detection method was adapted from Brochu et al. [26]; the representative ions for each individual congener are shown in Table 1. PCBs were separated on a 25 m×0.32 mm I.D. CPSil-8 column coated with a 0.25 μm film. The GC oven temperature program was: 60 °C, hold 2 min, rate 20 °C/min to 170 °C, hold for 6 min, rate 3 °C/min to a final temperature of 280 °C, hold for 10 min. Helium was employed as carrier gas, with a constant column flow of 1.0 mL/min. The injector was programmed to return to the split mode after 2 min from the beginning of a run. Split flow was set at 50 mL/min. The injector temperature was held constant at 270 °C. Trap, manifold and transfer-line temperatures were 250, 50 and 280 °C, respectively.

3. Results and discussion

3.1. Considerations on irradiation wavelength

The experiments were undertaken with low-pressure mercury lamps as the irradiation source (maximum emission at 254 nm), which are used extensively in PCB photochemistry [14–16], although with higher power than those employed in this study.

In order to make experiments more relevant to possible solar irradiation, light sources emitting at $\lambda \geq 300$ nm have also been widely used [11–14], but the disadvantage of this method is that relatively high PCB concentrations have to be utilised because of the low molar absorptivity of PCBs at such wavelengths [17]. Thus, the use of more-dilute solutions and low-pressure mercury lamps (more energetic radiation) is usually preferred. Since absorption is still into the same electronic band of the PCBs, it is expected that the photochemistry will remain the same as at the environmentally more interesting wavelengths [17].

3.2. Considerations on "on-fibre" photolysis

In a previous study [4] it was demonstrated that SPME fibres are very good supports for photodegradation studies. Those preliminary studies were considered extremely successful, not only because the SPME fibre was shown to work as a photoreaction support, but also because of the possibility of the photoproducts formed in such experiments being detected.

Blanks, dark tests and thermal tests were also carried out, demonstrating that no losses of analytes through volatilisation and/or thermal degradation occurred. Therefore, the clear differences observed when comparing PCB peak areas obtained in GC–MS with standard SPME (just extraction and desorption) and "on-fibre" SPME photolysis (extraction, "on-fibre" irradiation and desorption) were due to UV exposure.

Detailed analysis of chromatograms selected through representative ions for each group of PCBs (related to the number of chlorine atoms) confirmed the conclusions made from the RIC chromatograms and showed other results: the PCB-52 response does not change after photolysis and some non-added compounds appear in the chromatograms corresponding to irradiation experiments [4].

3.3. Preliminary experiments for direct aqueous photolysis

Since, in this set of experiments, the solutions were submitted to direct UV irradiation, the possibility of obtaining more polar photoproducts arose, especially hydroxyl derivatives [5,10]. For this reason, fibres consisting of polymers more adequate for polar compounds were tested: PDMS–DVB and Carboxen–DVB, together with the plain PDMS used in "on-fibre" experiments. Combinations of the following selected parameters were studied: direct immersion sampling–HS-SPME, ambient temperature/100 °C and with or without stirring and/or preheating the sample.

Carboxen fibre is not a good choice for PCB extraction, because it impedes the pursuit of the response change from the initial mixture. Moreover, we did not detect photoproducts, thus we decided not to use it. PDMS–DVB and PDMS fibres gave very similar results for these compounds, which confirms the conclusions arrived at in a comparative study carried out in our laboratory [27]. HS-SPME with PDMS fibre at 100 °C was selected to allow us to compare data from "on-fibre" photolysis with those from direct aqueous photolysis. Under these conditions, a standard SPME (reference) and two extractions after irradiating the solution for 15 or 60 min with UV light were carried out, plus a blank of ultra-pure water. The experiments were replicated twice. The chromatograms obtained demonstrated the existence of photodegradation in aqueous solution, as shown in Fig. 1.

3.4. Influence of irradiation time

To study the influence of irradiation time on the extent of photodegradation, the 10-PCB mixture was first extracted and then the fibre was subjected to UV light for the designed time: from 0 to 90 min (nine points). Two sets of experiments were run in GC–MS–MS mode to achieve better sensitivity. Area changes for each individual compound after UV exposure were evaluated separately, but PCBs 28 and 31 were coeluting peaks, so they were studied
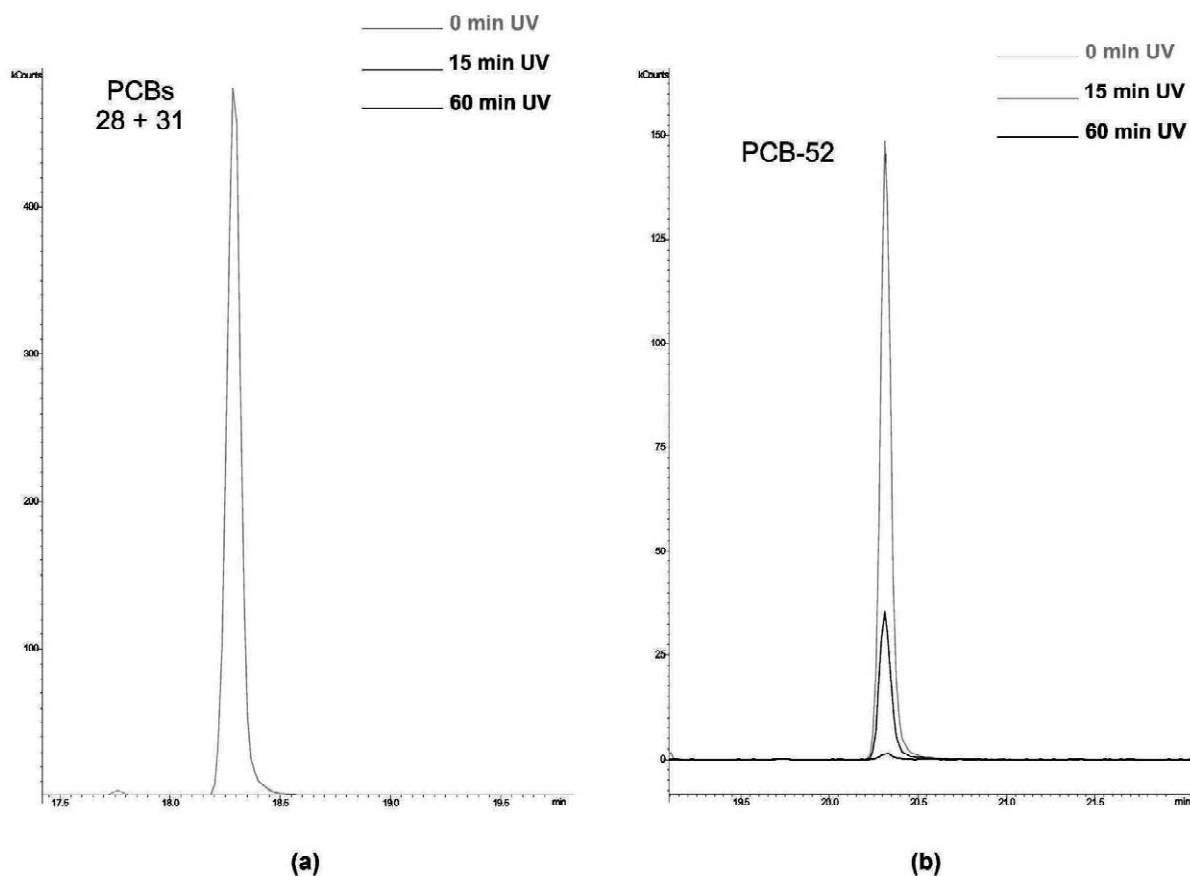
(a)

(b)

Fig. 1. Overlaid MS chromatograms selected through representative ions for each group of PCBs: 0 min (control, SPME without irradiation), 15 and 60 min UV irradiation in direct aqueous photolysis experiments. (a) Trichlorobiphenyls (m/z 256+258); (b) tetrachlorobiphenyl (m/z 290+292); (c) pentachlorobiphenyls (m/z 326+328); (d) hexachlorobiphenyls (m/z 360+362) and heptachlorobiphenyl (m/z 394+396).

together. For aqueous photolysis, the irradiation time range was the same and the experimental procedure was as described in the Experimental section.

Results for ''on-fibre'' photolysis [4] are summarised in Table 2. With short photolysis times (5 min), most of the studied PCBs disappeared almost completely, but there were exceptions: PCB 52 was the most resistant to photodegradation; among the pentachlorobiphenyls, PCB 101 was less degraded than PCBs 105 and 118; PCB 153 was, among the biphenyls with six chlorine atoms, the less photolyzed. The chemical structures of PCBs 52, 101 and 153 are closely related: chlorine substituents in positions 2, 2′, 5 and 5′ (this substitution pattern is known to present a lower relative reactivity). Work-

ing with cyclohexane, Lepine et al. [12] reached similar conclusions in homogeneous photolysis experiments.

The photodegradation of trichlorobiphenyls 28+ 31, pentachlorobiphenyls 105 and 118 and hexachlorobiphenyls 138 and 156 is so fast that, within 5 min of irradiation, the percentage left is lower than 5% of their initial concentration. All but PCB 138 possess one *ortho*-chlorine atom, which promotes the greatest photodecomposition efficiency [11,15]. With regard to PCB 138, it has two *ortho*-chlorines, which could contradict the preceding sentence, but it has three adjacent chlorine atoms (positions 2, 3 and 4), which facilitate the loss of chlorine in position 3 by steric congestion.
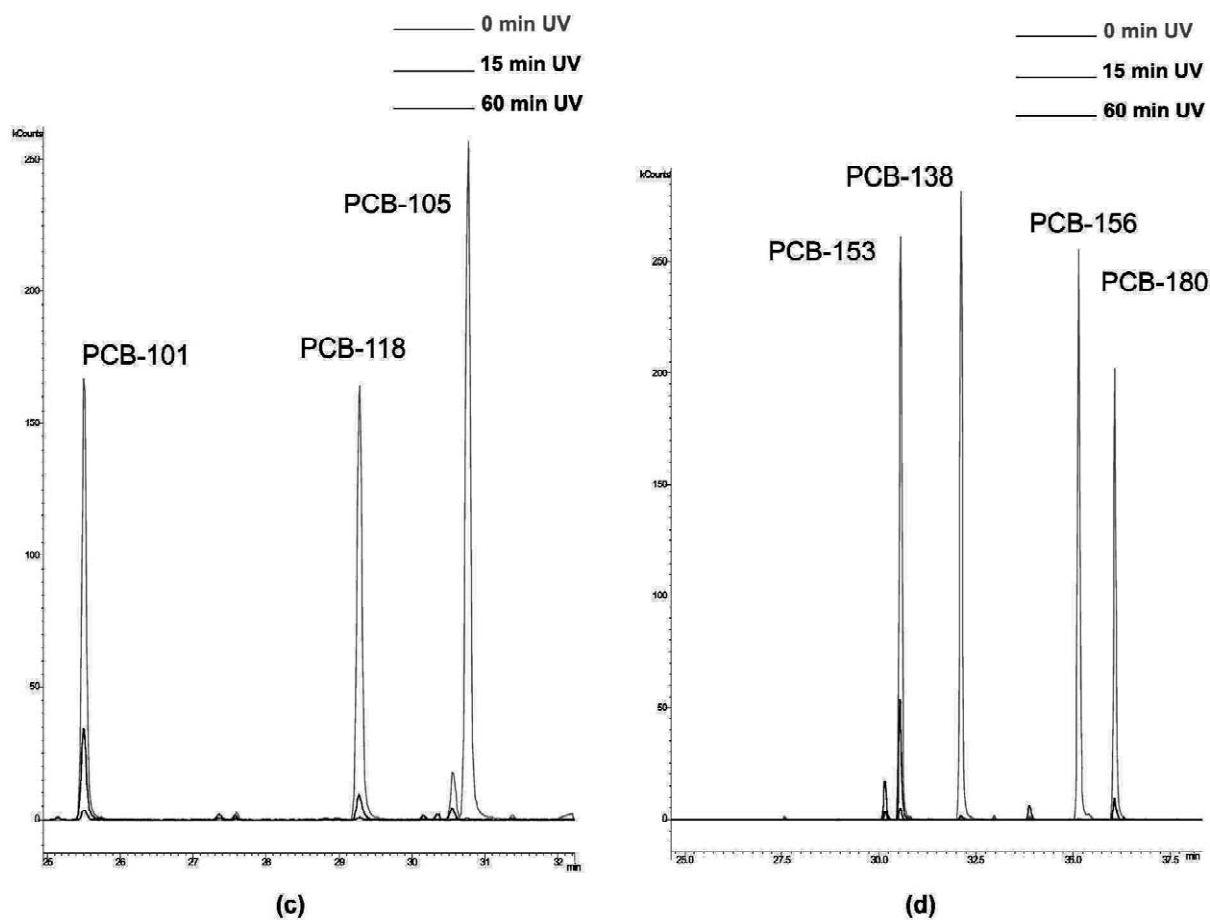
Fig. 1. (*continued*)

Table 2
Relative percentage of photodegradation for each PCB congener: "on-fibre" experiments

PCB	Relative percentage of photodegradation								
	Irradiation time (min)								
	0	2	5	10	15	30	45	60	90
28+31	0	84.1	97.5	98.1	98.5	98.5	99	98.9	98.9
52	0	2.5	1.2	1.1	3.5	18.5	32	31.8	47.7
101	0	18.5	44.6	64.9	74.5	95.6	100	100	100
118	0	73.8	95.5	97.1	98	98.8	99.7	99.6	100
153	0	7.9	58.6	86.8	94.6	99.1	99.6	99.6	99.8
105	0	96.9	98.7	98.5	98.9	100	100	100	100
138	0	89.5	98.6	99.1	99	99.3	98	100	98.6
156	0	96.5	98.6	99	98.9	99.1	99.8	100	100
180	0	54.7	90.4	97.6	97.9	98.9	98.9	98.9	99.5

The amount of all initial compounds remaining after 30 min UV light irradiation was under 1.5%, except for the less-reactive compounds: PCB-52 and PCB-101. When the maximum irradiation time (90 min) was used, only PCB-52 was detected (still 52%).

Table 3 shows equivalent data for the aqueous experiments. Photodegradation in solution was slightly slower than in ''on-fibre'' experiments for most of the compounds studied, the more significant differences being observed for PCBs 52, 101, and 153, the same PCBs that showed particular behaviour in ''on-fibre'' experiments. All detected tendencies in ''on-fibre'' photolysis were manifested here. The main differences were observed when comparing data for PCB-52 (2,2′,5,5′-tetrachlorobiphenyl): at an irradiation time of 30 min, there was still more than 80% of the compound remaining when the photolysis was carried out ''on fibre'', while with photolysis, more than 95% of the initial concentration disappeared. This ''on-fibre'' behaviour can be explained by the symmetrical congeners, such as PCB-52, as well as coplanar congeners, exhibiting lower photoreactivities. The results obtained here are very consistent with those obtained by Miao et al. [16] using hexane. It is highly probable that the solvent plays an important role in the aqueous photolysis of this compound.

The same discussion can be used for the half-life times ($t_{1/2}$), when the concentration is reduced to 50% of its initial amount. The values are between 0 and 2 min for most PCBs, except for PCB-101 (5–10 min) and PCB-153 (2–5 min), both in ''on-fibre''

and aqueous experiments. PCB-52 again shows a large difference between both approaches, with $t_{1/2}$ being longer than 90 min ''on fibre'' and in the 10–15 min interval for aqueous photolysis, suggesting the possible role of solvent molecules in the reaction mechanism.

3.5. Photodegradation pathways

The observed exponential decay suggests first-order or pseudo-first-order kinetic models with high reaction rates being the main decomposition mechanism observed in both systems of reductive dechlorination (Fig. 2). The photoproducts detected are new congeners not present in the initial mixture (see below), and some initial PCBs are formed via the dechlorination of more-chlorinated initial congeners, detected by unexpected peak area modifications [4]. Fig. 3 shows an example of this in aqueous photolysis: PCBs 52, 101 and 153 have a small shoulder between 2 and 5 min, which could suggest a dechlorination route from PCB-180 [12,16]. This heptachlorobiphenyl can lose the chlorine at position 3 of its more-substituted ring, giving PCB-153, which, in turn, can produce PCB 101 by the loss of another chlorine atom, which will produce PCB 52 (Fig. 2). These congeners present slower kinetics and are structurally related, as mentioned in the previous section, and this led us to deduce this pathway.

According to photochemical studies on PCBs [9,11,16] there are some general trends concerning the photoproducts obtained and the most important reaction pathways: (a) *ortho*-substitution greatly en-

Table 3
Relative percentage of photodegradation for each PCB congener: ''aqueous photolysis'' experiments

| PCB	Relative percentage of photodegradation								
	Irradiation time (min)								
	0	2	5	10	15	30	45	60	90
28 + 31	0	78.4	95.4	99.4	99.9	99.9	100	100	100
52	0	17.9	16.2	44.3	74	96.3	97	98.9	99.7
101	0	25.6	27.6	53.4	77.9	95.8	95.8	97.6	99.1
118	0	61.6	72.2	84.9	92.9	99.1	99.2	99.6	100
153	0	29.5	34.7	58.5	78.9	96.1	95.7	97.8	99.2
105	0	90	95.2	98.7	100	100	100	100	100
138	0	83.6	92.4	97.2	99	100	100	100	100
156	0	94	97.2	99.2	99.7	100	100	100	100
180	0	57.9	67.3	85	94.1	99.5	99.4	99.8	100
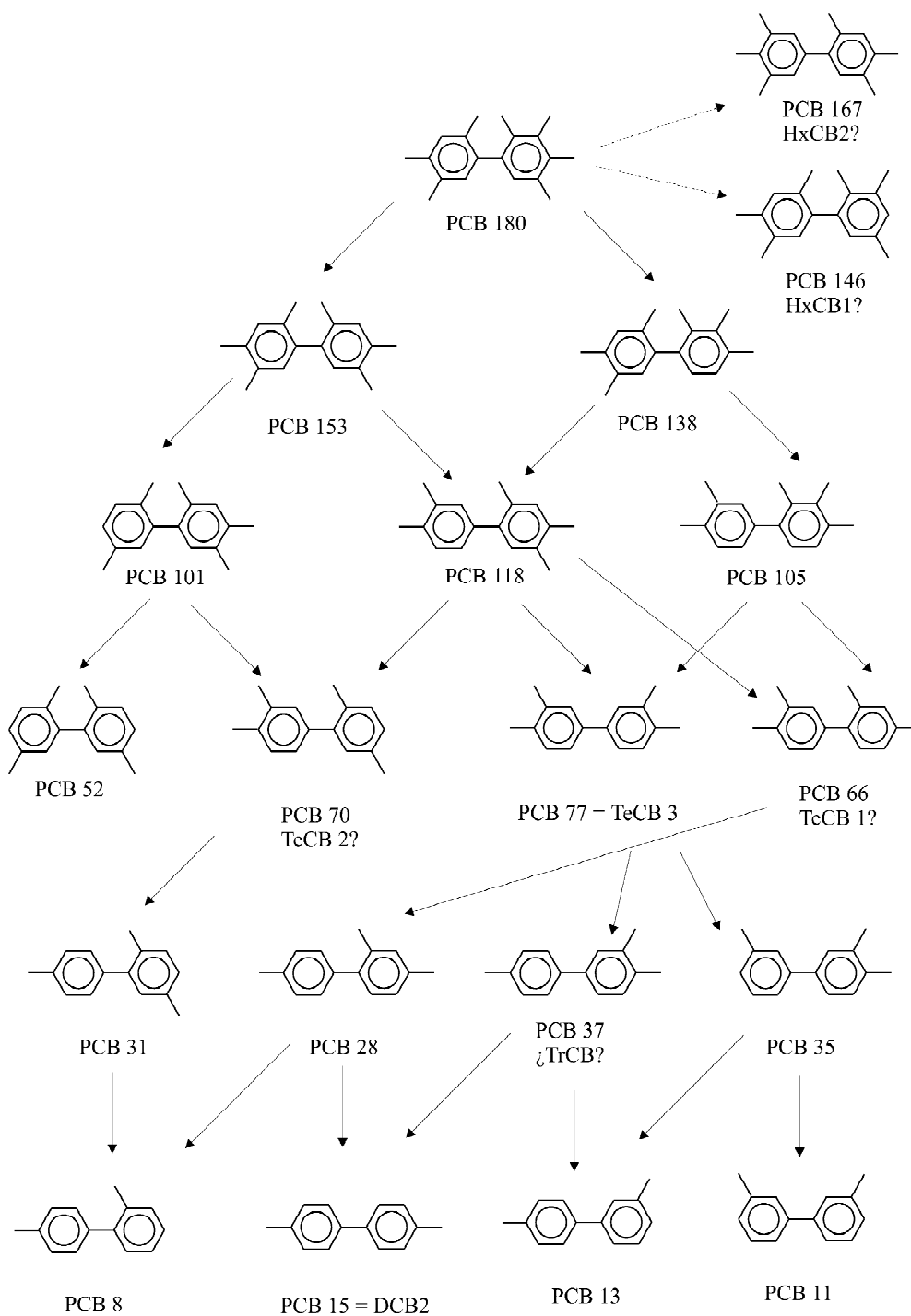
Fig. 2. Proposed photodegradation pathways. Each bond represents one chlorine atom.
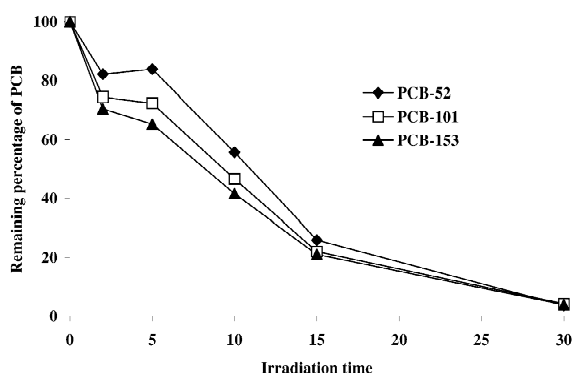
Fig. 3. Example of photogenerated compounds already present in the initial mixture.

hances photoreactivity (with the exception of PCB 52, probably due to the identical bond lengths of carbons with *ortho*-chlorines and with *meta*-chlorines); (b) *para*-chlorination increases the cleavage efficiency of an *ortho*-chlorine; (c) *meta*-chlorines decrease photoreactivity; and (d) photodechlorinations occur mainly on the more-substituted rings when the number of chlorine atoms on the two phenyl rings are unequal. All of these effects were detected in ''on-fibre'' experiments as well as in direct aqueous photolysis.

The suggested reaction pathway shown in Fig. 2 was constructed based on our experimental results and with the aid of information from the literature [12,16,28,29]. Photoproducts between question marks are only suggestions. Lores et al. [4] demonstrated that the best way to confirm photoproduct structures and the proposed photoreaction pathways is by the on-fibre SPME photolysis of individual congeners.

3.6. New photoproducts

The ''on-fibre'' SPME photolysis approach was then exploited to monitor the photolysis behaviour of PCBs and to determine the photoproducts produced at different irradiation times. Besides the possibility of studying the congeners already present in the initial mixture, some non-added PCBs could also be determined. Nine photoproducts were clearly detected in the first series of experiments: two dichlorobiphenyls (DCB1 and DCB2), one trichlorobiphenyl (TrCB1), three tetrachlorobiphenyls

(TeCB1, TeCB2, and TeCB3), one pentachlorobiphenyl (PeCB1) and two hexachlorobiphenyls (HxCB1 and HxCB2) [4]. It is well known that mass spectrometry is not able to distinguish between positional isomers, so it was only possible to estimate the number of chlorine atoms in the molecule.

Of course, the non-spiked compounds mentioned above also underwent photodegradation. It is difficult to assign new reaction pathways to these photochemically generated compounds, because all of them could be implicated in different routes. Some comments can be made about the behaviour noted in ''on-fibre'' experiments: most detected photoproducts have their maximum peak areas at short photolysis times and become undetectable at longer irradiation times, but at 90 min, DCB1 and DCB2 are still detectable, indicating that these less-chlorinated biphenyls are among the last links in the chain reactions.

Some polar photoproducts, together with less-chlorinated biphenyls, could be expected in aqueous photolysis. Nevertheless, only the latter were detected in this study, suggesting that the main photodegradation route under the experimental conditions assayed is reductive dechlorination as in the ''on-fibre'' scheme. The same nine photoproducts as described above were detected at their corresponding retention times, plus two new congeners that appeared when the irradiation time was 10 or 15 min: one trichlorobiphenyl (TrCB2) and one tetrachlorobiphenyl (TeCB4) (Fig. 4a and b). Nevertheless, these two PCBs and HxCB2 presented quite small peak areas (although sufficient for the compounds to be perfectly matched by a MS library search); this is the reason for not showing them in Fig. 4. The PCBs photogenerated in greater quantity were TeCB3, HxCB1 and PeCB1 (Fig. 4b). Again, these non-added species also have demonstrated photodegradation, making it difficult to outline the reaction pathways. After 90 min irradiation, the only detectable compounds were TeCB2 and TeCB3. It should be noted that aqueous photodegradation of DCB1 and DCB2 is faster than in ''on-fibre'' experiments (see above), the compounds disappearing after 30 and 60 min of UV irradiation, respectively.

The identity of DCB2 (PCB 15 or 4,4′-dichlorobiphenyl) and TeCB3 (PCB 77 or 3,3′,4,4′-tetrachlorobiphenyl) were confirmed in a previous
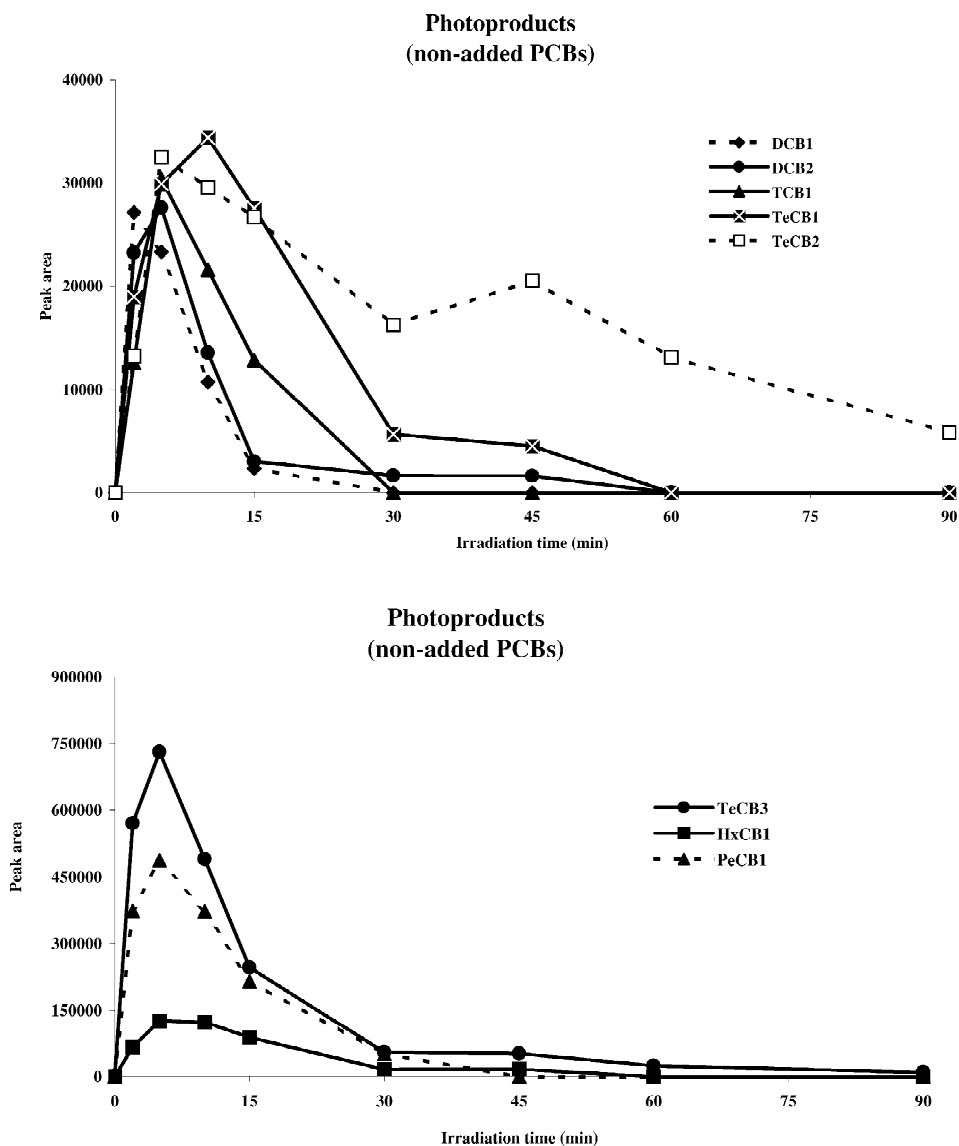
Fig. 4. Behaviour of non-added (photogenerated) PCBs at different irradiation times in direct aqueous photolysis experiments.

study [4]. PCB 77 is a coplanar congener with a chemical structure related to 2,3,7,8-tetrachlorodibenzodioxin (TCDD) and it is known to increase the toxic equivalents (TEQs) of solutions rapidly [16]. This was the most abundant polychlorobiphenyl among those generated photochemically in direct aqueous photolysis.

4. Conclusions

In aqueous photolysis, all PCBs were degraded more than 97% with an exposure time to UV light of 60 min. The behaviour observed in solution and ''on fibre'' was similar for all PCBs studied except PCB-52. The main decomposition mechanism observed

was reductive dechlorination in both sets of experiments.

SPME significantly simplifies photochemical studies of environmental organic pollutants, using it as an extraction technique to study photochemical processes in environmental matrices and as a support for photochemical studies: "on-fibre" photodegradation. Both approaches are suitable for studying the photodegradation kinetics of persistent organic pollutants and for analyzing photoproducts which are generated in situ in the fibre or extracted from the matrix with minimum sample manipulation. Photo-SPME mimics quite well the photochemical behavior of the pollutants in water samples and has enormous potential for in situ photochemical studies.

Acknowledgements

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