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Aqueous photolysis of the sunscreen agent octyl-dimethyl-*p*-aminobenzoic acid Formation of disinfection byproducts in chlorinated swimming pool water

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Abstract

The photochemical behavior of the sunscreen agent octyl-dimethyl-*p*-aminobenzoic acid (ODPABA) was studied in different aqueous solutions and under different conditions. ODPABA photolysis was performed under laboratory conditions using a xenon light source and under natural sunlight conditions in sea, swimming pool as well as in distilled water. The influence of dissolved organic matter (DOM) on the degradation kinetics was also studied in the presence of various concentrations of humic acids (HA). The phototransformation was shown to proceed via pseudo-first-order reaction in all cases and the reaction rates followed the order: distilled water > swimming pool water > seawater, depending mainly on the presence of dissolved organic matter that retarded the photolysis reaction. Kinetic experiments were monitored with HPLC/UV–DAD and the half-lives ($t_{1/2}$) varied between 1.6 and 39 h in simulated solar irradiation and between 27 and 39 h in natural sunlight conditions. The product distribution during illumination was strongly dependent on the constitution of the irradiated media. Irradiation of the aqueous ODPABA solutions gave rise to several transformation products that were isolated by means of solid-phase extraction (SPE) and identified using GC–MS techniques. These were formed mainly through dealkylation and hydroxylation reactions and were detected in all aqueous solutions investigated. In the case of swimming pool water some additional byproducts were isolated and were tentatively identified as chlorinated intermediates, formed by the subsequent chlorination of the parent molecule as well as other intermediates.

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1. Introduction

Sunscreen preparations deploy a variety of active ingredients with single or multiple aromatic structures,

and often with attached hydrophobic groups, able to attenuate the transmission of energetic solar photons that reach the surface of the earth. Although hydrophobic in nature, these substances have been recognized to undergo washing off from the skin surface in both laboratory and real-life investigations and thus being transferred to the water solution [1,2]. Recent reports on the determination of sunscreen agent residuals in

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indigenous organisms [3] and bathing waters have raised another important issue regarding their fate and behavior in the aqueous environment.

As these substances are designed to absorb a significant amount of solar energy, one can speculate that their fate in natural waters will be controlled by solar mediated mechanisms. It is nowadays well-established that photoinduced alteration processes are known to play an important role with regards to organic compounds degradation and may be a key factor in controlling their fate in natural waters. However, there is still a surprising dearth of information in the literature concerning the photochemistry of sunscreen agents, in illuminated aqueous solutions and especially in natural waters [5].

To date, only one major sunscreen agent, *p*-aminobenzoic acid (PABA), has been examined for its response in sunlight exposed water solutions with intriguing results [6–9]. It has been found that it produces singlet molecular oxygen (recognized for its cytotoxic effects) [9] while some byproducts have also been identified [6–8]. However, the declining use of PABA because of reports on its dermatological effects has triggered the use of other PABA-based substances (the most widely used derivative being the octyl-dimethyl-*p*-aminobenzoic acid, ODPABA) whose behavior is still largely unknown. ODPABA is currently used in many commercially available products, including sunscreens, with permitted levels up to 8% in finished products in the US and EU [10]. More dire still, although modeling of organic substances behavior under controlled laboratory conditions [11–13] is a very useful tool for environmental studies, there is an explicit demand to conduct phototransformation studies in real-life conditions [14] in order to account for environmental variations in physical and chemical parameters (temperature, sunlight intensity, etc.). Additionally, natural water composition may play an important role in inhibiting [15,16] or enhancing [17,18] the photolateration of organic compounds with dissolved organic matter (DOM) being of primary concern. Following this line of thinking, swimming pool waters, in which sunscreen residuals have been identified, impose a new field of research. Not only dissolved organic matter is present but chlorination of swimming pool waters may contribute to the formation of chlorinated organic compounds whose toxic effects are of primary concern. The involve-

ment of sunscreen agent residuals in this process is nevertheless utterly unknown.

In the same direction, a prerequisite for sound environmental field studies on sunscreen hydrochemistry is the provision of reliable analytical methods for their determination, at the nanomolar concentration levels. Reports on the development of analytical methods for determining UV-filters residues are still scant and only a few studies have been presented accomplishing their determination at the low $\mu\text{g/l}$ or ng/l levels [4,19–22]. In contrast to conventional LC methods for sunscreen detection [23,24], real-time analysis by GC techniques seem to offer an intriguing alternative. In our previous studies, we have undertaken a survey of sunscreen residuals in bathing waters at the sub-nanomolar concentration levels by exploiting the analytical merits of GC/FID and GC/MS techniques with the aid of solid-phase microextraction (SPME) and solid-phase extraction (SPE) procedures [4,20]. In this context, we now attempt to extend the analytical utility of LC and GC methods towards the investigation of the fate of these compounds and the determination of their phototransformation intermediates formed.

In a wider context, the aim of the present study is three-fold. First, it strives to decipher the prime mechanisms involved in the fate and environmental behavior of sunscreen agents in recreational waters and examine the effect of the ubiquitous dissolved organic matter in the results. Second, isolate and characterize the intermediate products, which are produced during the phototransformation process and third, identify the formation of disinfection byproducts in the chlorinated swimming pool water. By the force of example, ODPABA has been meticulously studied in various water matrices. The employment of both LC and GC techniques in the attempt to accomplish these objectives is also demonstrated.

2. Experimental

2.1. Chemicals

Octyl-dimethyl-*p*-aminobenzoic acid was purchased from Aldrich. Humic acid (HA) standard were purchased from Fluka (Steinheim, Germany). The solvents used ethyl acetate, dichloromethane, methanol, acetonitrile and water were of the highest

available purity (HPLC or GC grade) and were obtained by Pestiscan (Labsan Ltd., Dublin, Ireland) and Merck (Darmstadt, Germany). NaOCl, Na₂SO₃, and Na₂SO₄ were obtained from Merck. Styrenedi-vinylbenzene (SDB) extraction disks (47 mm) were supplied from 3M Empore (St. Paul, USA), and a conventional filtration apparatus was purchased from Supelco (Bellefonte, USA). C₁₈ cartridges (500 mg) were obtained from Chromabond (Machereu Nagel Gmd H&Co.).

2.2. Water sampling

Water samples from swimming pools as well as seawater from bathing areas from the coastal line of north-western Greece (Epirus) were collected in 2.5 l precleaned amber glass bottles sealed with screw caps lined with aluminum foil and stored at 4 °C prior to use. Seawater samples were used without previous treatment, filtration or sterilization. Residual chlorine in the swimming pool water was measured to 0.9 mg/l and brought to 2 mg/l with the addition of NaOCl. The residual Cl after completion of the reaction was removed by the addition of 100 mg/l Na₂SO₃. Total organic carbon (TOC) measurements was performed on a total carbon analyzer (TOC-5000 Shimadzu) using the high temperature catalytic oxidation method (HTCO) and its concentration was 2.53 mg/l for seawater and 1.81 mg/l for swimming pool water.

2.3. Chromatographic conditions

2.3.1. HPLC/UV–DAD

The decrease of ODPABA concentration during photolysis was monitored using a Shimadzu on-line degassing system DGU-14A coupled to a FCV-10AL controller unit and a LC-10AD high-pressure solvent delivery pump, with a 20 µl sample loop injector. A Shimadzu SPD-M10A UV/diode-array detector operating under the chromatography software Class-VP version 5.0 was used for recording chromatographic peaks. The column material was a Discovery C₁₈ (Supelco), with particle size of 5 µm (25 cm × 4.6 mm i.d.) and preceded by a guard column of the same material (8 mm × 3 mm). Isocratic elution with a mobile phase composed of water/acetonitrile (20/80% v/v) was used for the elution of ODPABA from the column. Column temperature was set at 30 °C and

the data collection was performed by obtaining one spectrum per second with resolution of 4.0 nm and no smoothing.

2.3.2. GC–MS

A GC–MS, QP 5000 Shimadzu instrument equipped with capillary column DB-5-MS (30 × 0.25) mm × 0.25 µm, containing 5% phenyl–95% dimethylpolysiloxane (J&W Scientific, Folsom, CA, USA) was used for the identification of the transformation products under the following chromatographic conditions: injector temperature 250 °C, oven temperature program from 55 to 200 °C at 5 °C/min, from 200 to 210 °C (held for 2 min) at a rate of 1 °C/min and to 270 °C (held for 3 min) at 10 °C/min. Helium was used as the carrier gas at 1 ml/min. The interface was kept at 290 °C. The MS was operated in electron impact mode with an ionization potential of 70 eV and the spectra were obtained in full scan mode. The injector mode was splitless and the injection volume was 3.0 µl.

2.4. Photodegradation studies

Photodegradation studies of ODPABA were conducted under natural sunlight in three different matrices (distilled, swimming pool and sea water) in capped duran glass reservoirs in the Ioannina area (University campus, roof terrace of the Department of Chemistry) during June 2002.

Laboratory experiments were carried out in 6.5 cm diameter cylindrical duran glass UV-reactor by exposing 50 ml of the aqueous solutions of ODPABA (0.1 mg/l) in distilled, swimming pool and sea water, under artificial solar irradiation. The irradiation was carried out using a Suntest CPS+ apparatus from Atlas (Gelnhausen, Germany), equipped with a xenon arc lamp as reported previously [25].

In order to examine the effect of dissolved organic matter, irradiations were also conducted in the presence of various concentrations of humic acids (1.0–20.0 mg/l) using the suntest apparatus, the same reactor and initial concentration of ODPABA.

Meanwhile, control experiments in the dark (blank experiments) under the same conditions and initial concentrations of ODPABA were carried out in parallel for comparison without the application of light.

2.5. Quantification and extraction procedure

Aliquots of 5 ml were taken out from the reservoirs (outdoor experiment) and the reactor (laboratory experiment) at predetermined times of irradiation and were pre-concentrated (50-fold) with the aid of a J.T. Baker SPE apparatus, using the C₁₈ cartridges. The procedure consisted of washing the cartridge with 5 ml of dichloromethane:ethyl acetate (1:1 v/v), then conditioned with 5 ml of methanol followed by 5 ml of distilled water. The 5 ml of the irradiated sample was percolated through the cartridge and dried under vacuum. ODPABA was extracted with two consecutive 3 ml aliquots of the solvent mixture dichloromethane:ethyl acetate (1:1 v/v). The extracts were evaporated to dryness under a gentle stream of nitrogen and re-dissolved in 0.1 ml of methanol. A 50 µl aliquot was injected to the liquid chromatograph in order to follow the reaction kinetics. Quantification was performed with external calibration curves constructed under the same experimental procedure. The data reported hereafter refer to the pre-concentrated extracts unless otherwise stated. All experiments were carried out in triplicate.

For the identification of transformation products, the remaining solutions (≈700 ml) of natural sunlight irradiation experiments and 50 ml of aqueous solutions irradiated under simulated solar light were extracted by an off-line solid-phase extraction system at the end of total irradiation time. SDB extraction disks were used as the sorbing phase since they provide good recoveries for medium polar pesticides and due to the efficiency in the analysis of intermediates resulting from photolysis processes [25–27]. Prior to extraction the disks were activated with 10 ml of acetone for 2 h while 3.5 ml (outdoor experiment) and 0.25 ml (suntest experiment) of methanol modifier was added to the residues to allow better extraction. The SDB extraction disks were then placed on a sintered glass filter funnel apparatus attached to a vacuum source. A 5 ml volume of solvent mixture, dichloromethane:ethyl acetate (1:1 v/v) was added to the filter funnel and the disks were dried for 3 min. Then, 5 ml of methanol was added and after almost all the methanol was drawn through the disk [28], 10 ml of deionized water was added. Then, 50 and 700 ml volume of the water samples were added at flow rate of 2.5 and 20 ml/min, respectively. After the water sample had passed through,

the vacuum was left on for 10 min to allow the disk to become dry. The filtration system was put in a reservoir to receive the extract containing ODPABA as well as the transformation intermediates. The extraction was conducted with 3 × 10 ml of solvent mixture dichloromethane:ethyl acetate (1:1 v/v) as eluting system. The solvents and sample were drawn through the disks at a rate of approximately 1 ml/min. The extracts were then dried over anhydrous sodium sulfate, concentrated to 0.1 ml under a gentle stream of nitrogen and further analyzed into the GC–MS instrument. The use of GC–MS is advantageous in that it is highly sensitive (even the minor peaks are identified through their MS spectra) and less time consuming since it allows a rapid analysis of the photolysis samples.

2.6. Calculation of half-life

The calculation of half-life time was performed using the first-order rate equation:

$$C_t = C_0 e^{-kt}$$

where C_t represents the concentration at time t , C_0 the initial concentration and k the rate constant (slope).

The phototransformation constants in the case of outdoor experiment (natural solar irradiation) were calculated by subtracting the exponents of degradation curves representing the apparent degradation (k_{app}) and the degradation owed to hydrolysis, volatilization and biodegradation (k_{dark} , dark experiment). In this way the considered k_{phot} constants and the half-lives $t_{1/2}$ refer to the real photochemical reaction excluding the contribution of other factors ($k_{phot} = k_{app} - k_{dark}$, $t_{1/2} = \ln 2/k_{phot}$). In laboratory conditions, results have shown no sign of UV-filter degradation in the dark (blank experiments) showing that the decrease in the concentrations of ODPABA during simulated solar irradiation, is due to photochemical processes.

3. Results and discussion

Before proceeding with the illumination of ODPABA, the recovery offered by the proposed SPE/LC–DAD method was investigated in order to assess and verify the validity of our observations. The recovery of 0.02 mg/l ODPABA ranged from 97.6% in seawater to 101.2% in swimming pool water while

distilled water extraction efficiency was maintained above 98% in all samples analyzed. Calibration curves were rectilinear for the concentration range between 2–10 $\mu\text{g/l}$ ($R^2 = 0.991$) and 10–100 $\mu\text{g/l}$ ($R^2 = 0.995$), respectively, yielding detection limits ($S/N = 3$) as low as 0.3 $\mu\text{g/l}$.

3.1. Phototransformation kinetics

The photodegradation kinetics of ODPABA disappearance were of first-order in all cases. The net first-order rate constants (k_{phot}) and the half-lives ($t_{1/2}$) for natural and simulated solar irradiation are listed in Table 1.

From the degradation curves (Figs. 1 and 2) it can be seen that ODPABA reaction rates followed the order: distilled water > swimming pool water > seawater depending on the constitution of the irradiated media. After 60 h of daylight exposure 86, 83 and 80% of ODPABA was degraded in distilled, swimming pool and seawater, respectively, while more than 99, 96 and 92%, respectively, degraded within 10 h under simulated solar irradiation. The rate constant data show that the presence of organic matter in the water samples possibly inhibits the degradation rate of ODPABA.

In order to verify the effect of DOM, experiments with the same initial concentration of ODPABA and various concentrations of HA in distilled water, were

conducted under simulated solar irradiation (Fig. 3). Our results reveal that as the concentration of humic acids increases, the degradation kinetics of ODPABA decreases, compared to direct photolysis in distilled water. Experiments conducted with concentrations 1.0, 2.5, 5.0, 10.0 and 20.0 mg/l of HA in 10 h photoperiod resulted in 98, 94, 89, 78 and 66% disappearance of ODPABA.

The observed retardation on the photodegradation of ODPABA in the presence of organic matter can be explained by a competition process between DOM and ODPABA for the available photons, thus slowing down the direct photochemical reaction of ODPABA (optical filter effect) [29]. Also, particulate matter such as sediment particles and microorganisms suspended in the water column may scatter incident light, greatly reducing penetration of light beneath the surface. Another reason may be a partial binding between DOM and ODPABA by hydrophobic partitioning or weak van der Waals forces, and this fraction was never available to photolysis action. The retarded photodegradation rate in seawater is also consistent with $\bullet\text{OH}$ scavenging by chloride ions [30].

When comparing the rate constants with HA concentrations, the influence was not proportional since a 20-fold increase in HA resulted in only a 15–75% decrease in the reaction rate. This could be explained by a combination of “optical filter” effect coupled with a sensitization effect by the DOM phase. Photosensitized reactions involving energy, electron and hydrogen atom transfer reactions as well as photosensitized reactions with photochemically generated free radicals have been widely described to initiate the indirect photodegradation of organic contaminants in aqueous solutions [31,32]. In addition to dissolved organic matter (such as humic and fulvic acids), $\bullet\text{OH}$ radicals that are generated in natural waters by the photolysis of nitrate and nitrite as well as in waters containing sufficiently high metal ion concentration—through ligand to metal charge transfer reaction and photo Fenton chemistry—have been shown to sensitize the phototransformation of organic contaminants in aqueous solutions [33–35].

Although the irradiance of the sun energy and the one for the Xe lamp cannot be compared, the phototransformation rates calculated under simulated sunlight irradiation were 15 times greater than that of natural sunlight irradiation, providing more realistic environmental transformation rates [36].

Table 1
Photolysis kinetic parameters of ODPABA in different aqueous media

Photolysis	$t_{1/2}$ (h)	k_{phot} (h^{-1})	R^2
Natural solar irradiation (outdoor)			
Distilled water	27	0.0258	0.984
Sea water	39	0.0176	0.979
Swimming pool water	32	0.0220	0.981
Simulated solar irradiation (suntest)			
Distilled water	1.6	0.4433	0.994
Sea water	2.7	0.2526	0.995
Swimming pool water	2.1	0.3239	0.997
Simulated solar irradiation (suntest) ^a (mg/l)			
HA ^b , 1.0	1.8	0.3791	0.996
HA, 2.5	2.4	0.2841	0.993
HA, 5.0	3.2	0.2156	0.987
HA, 10.0	4.5	0.1530	0.973
HA, 20.0	6.3	0.1097	0.994

^a Distilled water.

^b Humic acids.

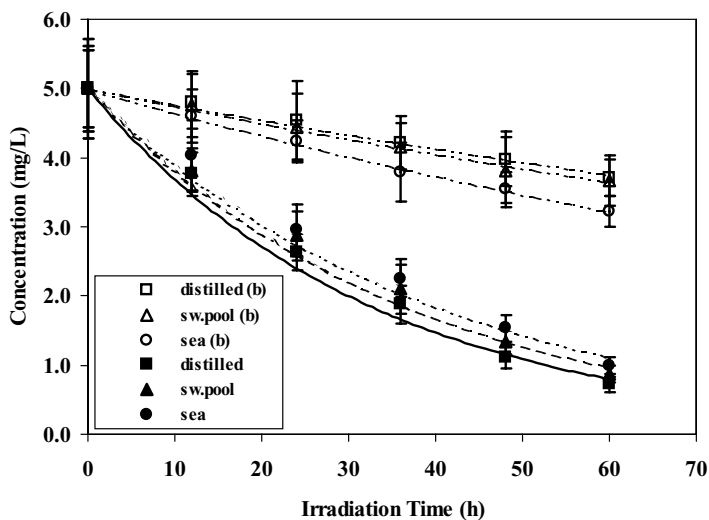


Fig. 1. Photodegradation of ODPABA in distilled, sea and swimming pool water under environmental conditions; (b): blank experiment.

In a previous work, Vanquerp et al. [37] reported that ODPABA was relatively stable during illumination (laboratory conditions) with a half-life of $t_{1/2} = 3287$ min. The differences (compared to our values) might be rationalized by differing sunlight intensities (6.45 and 1.47 mW/cm², for UV-A and UV-B, respectively, in reference [37], 750 W/m² in our study), as well as consideration of UV-reactor characteristics

(glass type and thickness, geometric shape) and sample volume used.

3.2. Transformation products

Fig. 4a is a typical total ion chromatogram (TIC) obtained by GC-MS for a SPE extract of ODPABA solution after 60 h of solar irradiation in seawater. Similar

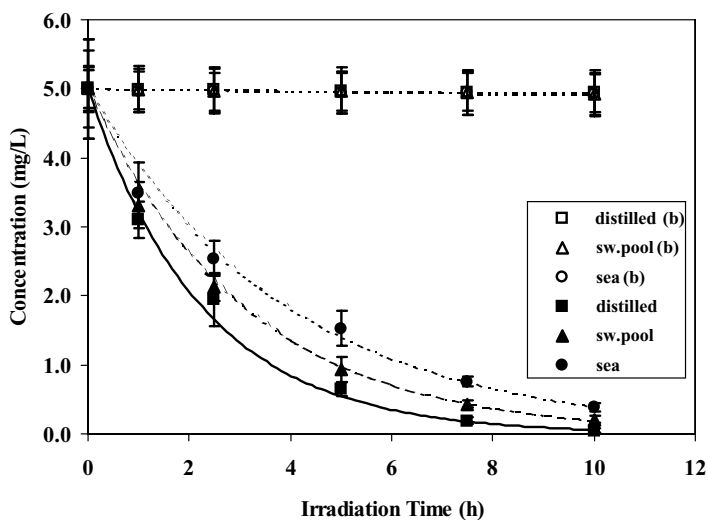


Fig. 2. Photodegradation of ODPABA in distilled, sea and swimming pool water under simulated solar irradiation; (b): blank experiment.

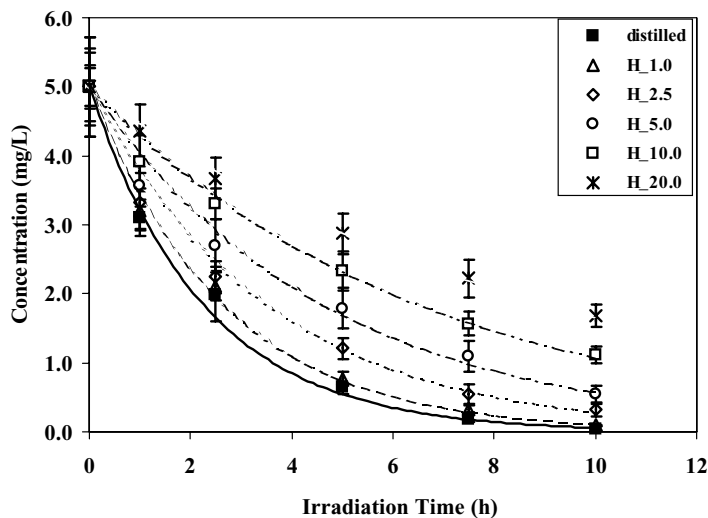


Fig. 3. Photodegradation of ODPABA in various concentrations of humic acids in distilled water under simulated solar irradiation.

chromatograms were also obtained in distilled water when natural or artificial solar irradiation was used as the light source. Up to four compounds could be detected as possible transformation intermediates. Three of them were identified while the fourth was consid-

ered as possible transformation intermediate since its amounts increased in the early steps of photolysis and then decreased with longer irradiation time. The mass spectra of the unlabelled peaks were not characteristic enough to enable us to propose the structure. The

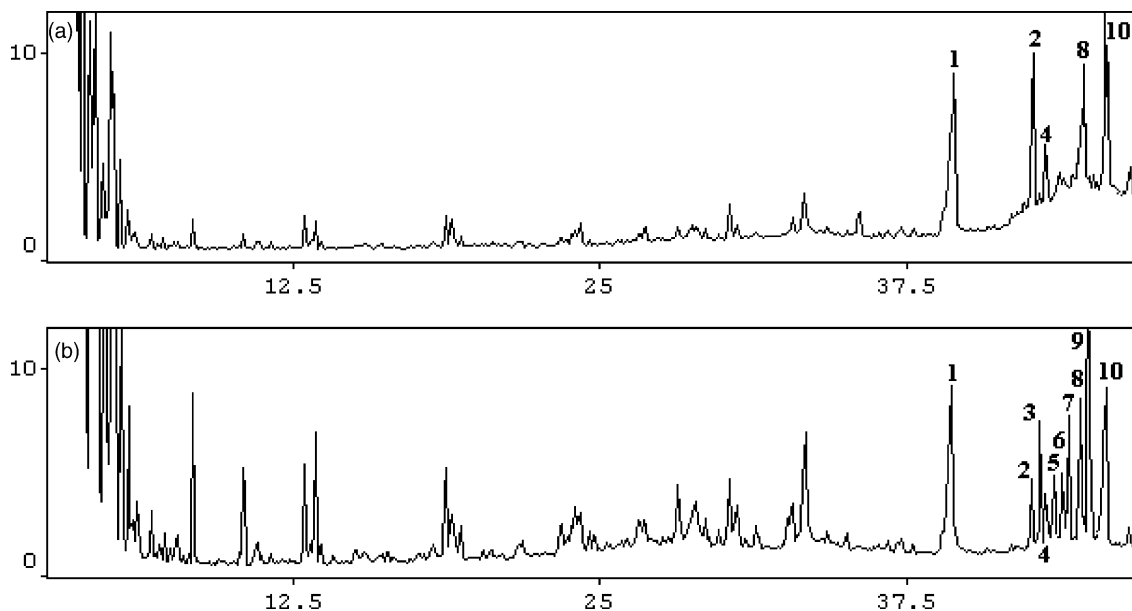


Fig. 4. Total ion chromatogram of ODPABA phototransformation in (a) seawater and (b) chlorinated swimming pool water, using SPE and GC–MS analysis (outdoor experiment).

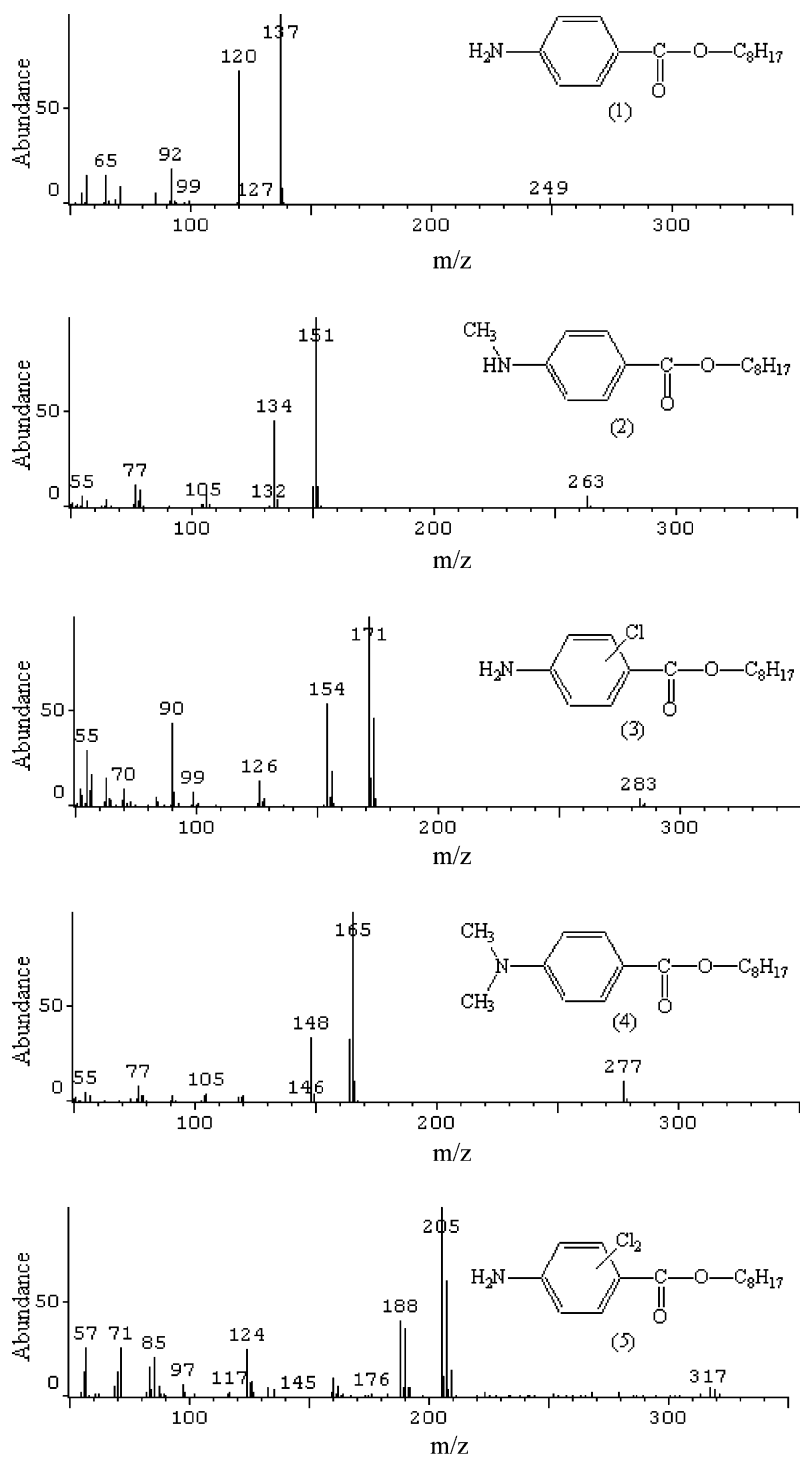


Fig. 5. Mass spectra of degradation products formed during ODPABA photodegradation in chlorinated swimming pool water.

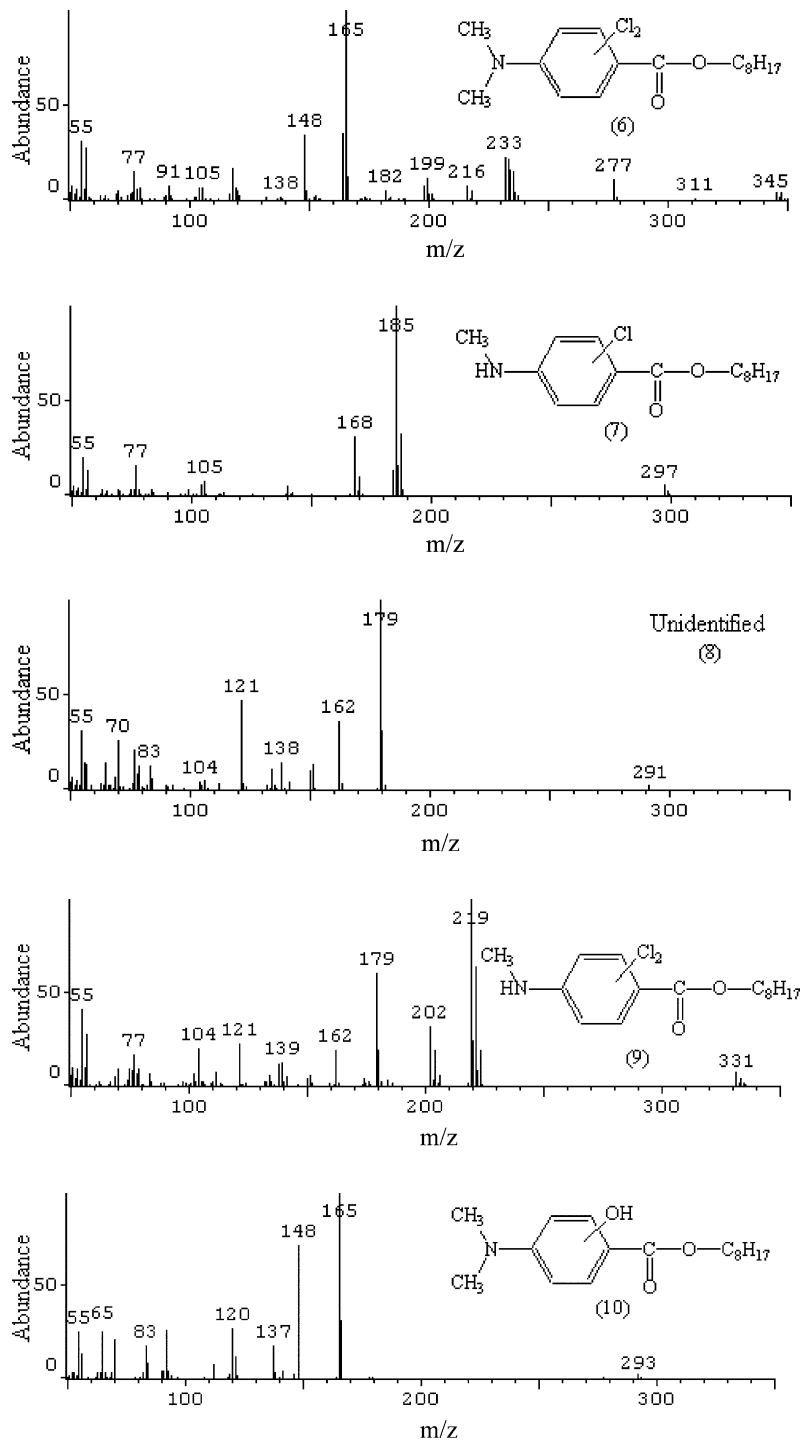


Fig. 5. (Continued).

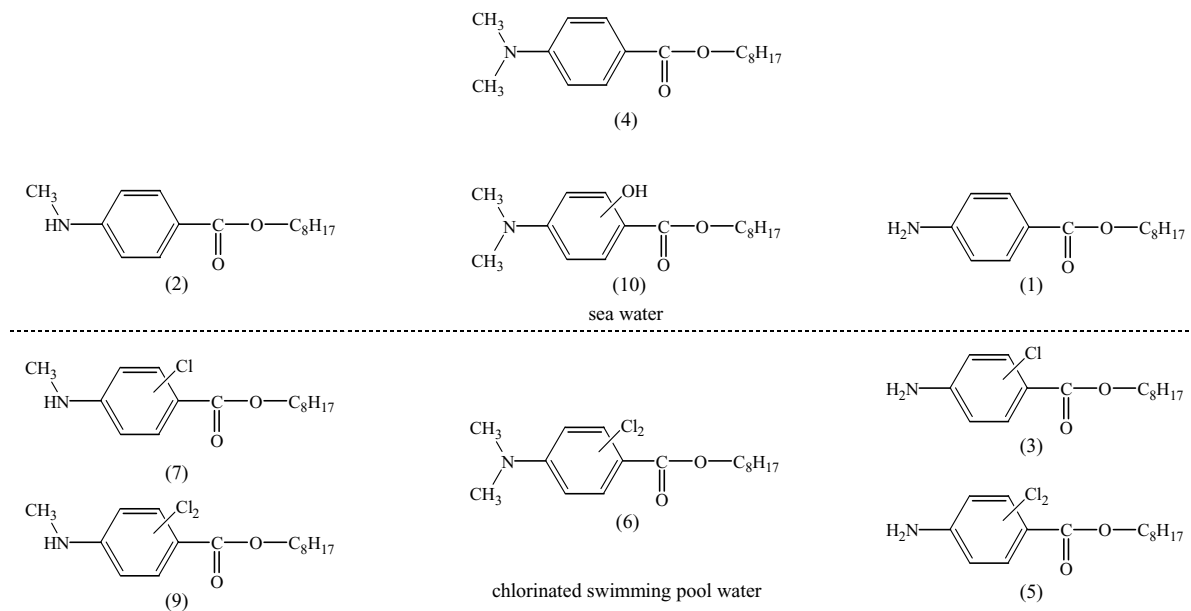


Fig. 6. Major photodegradation intermediates of ODPABA in seawater and in swimming pool water.

GC/MS characteristics of the reaction byproducts and their structure are presented in Table 2 and Fig. 5, respectively.

Compound (10) appearing at $R_t = 45.6$ min was identified as the hydroxy derivative of ODPABA since it exhibited a molecular ion at $m/z = 293$ and similar to ODPABA ions corresponding to the addition of OH group in the aromatic ring. Compounds (1) and (2) with retention times 39.5 and 42.7, respectively, were identified as the dealkylated

derivatives of ODPABA. Compound (2) associated to octyl-methyl-*p*-aminobenzoic acid, exhibited a molecular ion peak at $m/z = 263$ as well as fragments at $m/z = 151$ and 134 corresponding to the loss of the methyl group of the parent molecule. Compound (1), octyl-*p*-aminobenzoic acid that was also identified by interpretation of the mass spectra, exhibited a molecular ion at $m/z = 249$ and fragments at $m/z = 137$ and 120 corresponding to the loss of two methyl groups of the starting molecule. Chromatographic

Table 2

GC–MS–EI retention times (R_t) and spectral characteristics of ODPABA major byproducts

Number	Compound	R_t (min)	Mass spectrum peaks
1 ^a	Octyl- <i>p</i> -aminobenzoic acid	39.5	249, 137, 120
2	Octyl-methyl- <i>p</i> -aminobenzoic acid	42.7	263, 151, 134
3	Octyl- <i>p</i> -amino-chloro-benzoic acid	42.9	283, 285, 171, 173, 154, 156
4	Octyl-dimethyl- <i>p</i> -aminobenzoic acid (ODPABA)	43.1	277, 165, 148
5	Octyl- <i>p</i> -amino-dichlorobenzoic acid	43.3	317, 319, 205, 207, 209, 188, 190
6	Octyl-dimethyl- <i>p</i> -amino-dichlorobenzoic acid	43.9	345, 347, 233, 235, 237, 216, 218
7	Octyl-methyl- <i>p</i> -amino-chloro-benzoic acid	44.0	297, 299, 185, 187, 168, 170
8	Unidentified	44.7	291, 179, 162, 151
9	Octyl-methyl- <i>p</i> -amino-dichlorobenzoic acid	44.9	331, 333, 335, 219, 221, 223, 202, 204, 206
10	Octyl-dimethyl- <i>p</i> -amino-hydroxy-benzoic acid	45.6	293, 165, 148, 137, 120

^a Corresponding number in Figs. 4–6.

data indicated the presence of one more intermediate, compound (8) found at $R_t = 44.7$ min that could not be identified however were regarded as possible transformation product because it was detected in all experiments and its concentration increased and decreased as a function of the reaction time.

Concerning the photoproduct analysis in swimming pool water five more intermediates were detected (Figs. 4b and 6). These compounds were identified by interpretation of the mass spectra and seem to be formed by the subsequent chlorination of the previously mentioned compounds as well as of the parent molecule. Compound (3) appearing at $R_t = 42.9$ min, exhibited a molecular ion at $m/z = 283$ and fragments at $m/z = 171$ and 154 and is associated to octyl-*p*-amino-chloro-benzoic acid. The dichloro intermediate, compound (5) found at $R_t = 43.3$ min, exhibited a molecular mass ion at $m/z = 317$ and fragments at $m/z = 205$ and 188 and was identified as octyl-*p*-amino-dichlorobenzoic acid. There is also one more pair of peaks, compounds (7) and (9) that correspond to mono- and dichloro substitutions of compound (2) and are associated to octyl-methyl-*p*-amino-chloro-benzoic acid ($R_t = 44.0$ min) and octyl-methyl-*p*-amino-dichlorobenzoic acid ($R_t = 44.9$ min), respectively. Compound (6), octyl-dimethyl-*p*-amino-dichlorobenzoic acid, appearing at $R_t = 43.9$ min, was formed by the addition of two chlorine atoms in the aromatic ring of the parent compound, exhibiting a molecular ion at $m/z = 345$, 347 as well as fragments at $m/z = 233$, 235 , 237 , 216 and 218 , characteristic to the isotopic pattern of chlorine atoms.

4. Conclusions

In retrospect, the main objectives of this research, that of revealing the phototransformation mechanisms involved in the fate of sunscreen agents and identify their major byproducts, have been met within the confines of the present study. It was demonstrated that the UV absorbing compound ODPABA degrades photochemically in the aquatic environment leading to the formation of several photoproducts. The transformation rates were lower in sea and swimming pool water compared to distilled water showing a strong dependence on the composition of the water sample. The

presence of DOM retards the rate of the photolysis while the formation of various transformation products was followed via first-order reactions. Four photoproducts could be isolated from seawater using SPE and GC–MS techniques. However, more compounds are formed in the chlorinated swimming pool water that are suspected for toxic effects, showing that sunscreen residues may be an important source for the formation of disinfection byproducts.

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