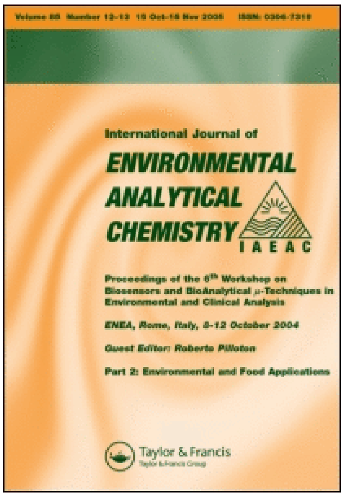

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Gustavo A. Peñela[a]; Imma Ferrer[a]; Damià Barceló[a]
[a] Department of Environmental Chemistry, Barcelona, Spain

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IDENTIFICATION OF NEW PHOTODEGRADATION BYPRODUCTS OF THE ANTIFOULING AGENT IRGAROL IN SEAWATER SAMPLES

GUSTAVO A. PEÑUELA, IMMA FERRER and DAMIÀ BARCELÓ*

Department of Environmental Chemistry, IIQAB-CSIC, c/Jordi Girona 18–26 08034 Barcelona, Spain

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A photodegradation study for Irgarol was carried out in order to investigate several products of degradation formed in different environmental matrices and under different conditions. Deionized water, groundwater and seawater samples, spiked at 30–100 µg/L with Irgarol, were irradiated using a xenon arc lamp and/or sunlight. Aliquots of the spiked water samples were taken at different times of irradiation and compounds were isolated from the water samples by means of solid-phase extraction (SPE) using either C_{18} or PLRP-s cartridges. Separation and detection of the compounds was accomplished by several analytical methodologies such as liquid chromatography-diode array detection (LC-DAD), liquid chromatography-electrospray ionization/mass spectrometry (LC-ESI/MS) and gas chromatography-mass spectrometry (GC-MS). Four new byproducts, with molecular weights of 167, 197, 207 and 213, were identified in this photodegradation study. When the photolysis was carried out with xenon lamp, half-lives of Irgarol were 103.8, 125.4 and 107.5 minutes in deionized water, groundwater and seawater, respectively. In seawater samples, a 98% of degradation was observed for Irgarol, after 217 hours of solar irradiation, being the main byproduct formed that corresponding to $M_w = 213$. On the other hand, the use of two different sensitizers -(TiO_2/H_2O_2), ($FeCl_3/H_2O_2$)- was also evaluated in deionized water samples containing Irgarol. These experiments were carried out in order to evaluate the use of these two sensitizers for decontamination of polluted waters.

Keywords: Irgarol; seawater; photodegradation

INTRODUCTION

The herbicide 2-(methylthio)-4-(*tert*-butylamino)-6-(cyclopropylamino)-*s*-triazine (tradename, Irgarol 1051) is used in antifouling paints as a biocide agent in substitution to the tributyltin (TBT) and copper-based agents. This compound is

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* Corresponding author. Fax: 34–93–2045904. E-mail: dbcqam@cid.csic.es

used in tin-free antifouling paint formulations that are mainly based on copper and zinc metal oxides. The herbicide is added in order to inhibit the primary growth of copper-resistant fouling organisms such as algal slimes and the growth of seaweeds. Few data concerning Irgarol 1051 contamination of the aquatic environment are available. For example, important coastal concentrations of Irgarol have been found in areas of high yachting activity, particularly in marinas and sportive harbors [1–4]. Recently, concentrations of Irgarol and diuron in the ng/L level were detected in a pilot monitoring study carried out in the coastal Mediterranean area of Catalonia during 1996–1997 [5].

The degradation of contaminants in water is an area of research interest and, in this sense, sunlight photoalteration processes are known to play an important role. Moreover, the study of contaminant photochemical behavior is a key issue in terms of the formation of toxic transformation products. Information on degradation products is necessary to understand the environmental fate of pesticides and to establish important degradation pathways, which will allow us to get a better knowledge of the transformation of target compounds in the environment.

Irgarol degradation studies have been reported in the literature, such as the biodegradation work of Liu et. al [6]. Photodegradation studies of this compound have been recently reported by Okamura et al. [7]. Since degradation studies are difficult to carry out under real conditions, natural sunlight photodegradation processes are usually compared with those obtained under controlled conditions, generally using xenon arc lamp [7–11].

Another way to study the photodegradation of organic compounds in water samples is by means of sensitizers that accelerate the process of degradation and it can be used for decontamination purposes. In this sense, the photodegradation using sensitizers such as TiO_2 or Fenton's reagent is an area of environmental interest for the treatment of contaminated natural waters. The degradation using photosensitizers is a faster reaction than photolysis because these compounds accelerate the formation of very reactive species, such as hydroxyl radicals, which in turn attack the organic contaminants. The Fenton's reagent, which is a mixture of hydrogen peroxide and ferrous iron, has been used to decompose a wide range of organic compounds, such as chlorinated pesticides [8–12], phenols [13], chlorinated phenols [14, 15], nitrotoluenes [16], etc. The oxidizing power of the reagent can be greatly enhanced by irradiation with UV light [12], and, then the mineralization of organic compounds is very fast. The photodegradation with Fenton's reagent has been carried out using Fe^{2+} or Fe^{3+} since both react with hydrogen peroxide [12]. On the other hand, photocatalysis with TiO_2 has been used to degrade several organic compounds, such as chlorinated pesticides [8–11, 17, 18], insecticides [19, 20], phenols [13], chlorophenols [21] and PCBs [22]. The rates and efficiencies of photoassisted degradation with TiO_2 are significantly improved in the presence of oxygen or by the addition of several inorganic oxidizing species, such as peroxydisulfate, periodate and peroxides [23].

The objectives of this work were (1) to determine the photodegradation kinetics of Irgarol 1051 in deionized water, groundwater and seawater by using natural photolysis and xenon arc irradiation, (2) to detect new photodegradation products formed, by GC-MS (EI) and LC-ESI/MS, and (3) the use of photosensitizers such as TiO_2/H_2O_2 and $FeCl_3/H_2O_2$ in combination with light irradiation, with the purpose to decontaminate water samples containing Irgarol. To our knowledge this work represents the first photodegradation study, under environmental conditions, of the antifouling agent Irgarol.

EXPERIMENTAL SECTION

Chemicals

Irgarol 1051 (99%) and the byproduct (2-methylthio-4-*tert*-butylamino-*s*-triazine) were obtained from Ciba-Geigy (Barcelona, Spain), Diuron from Promochem (Wesel, Germany) Iron (III) Chloride 6-hydrate (98–102%) from Panreac (Barcelona, Spain) and Titanium dioxide P25 from Degussa (Japan). Hydrogen peroxide (30% solution) was from Foret (Barcelona). HPLC-grade solvents acetonitrile, methanol, and water were purchased from Merck (Darmstadt, Germany). Ethyl acetate and ammonium acetate were obtained from Panreac (Barcelona, Spain). Deionized organic-free water (pH 8.3), prepared with a Milli-Q system from Millipore-Waters Co, groundwater (pH 7.6, 344 mg/L of sulfates, 360 mg/L of chlorides, 68 mg/L of nitrates, 260 mg/L of Ca, 78 mg/L of Mg, 1.6 mg/l of TOC, conductivity 2050 µmhos/cm), and seawater samples, from Masnou, Catalonia, Spain (pH 8.0), were used for the study of the degradation kinetic of Irgarol.

The SPE cartridges used consisted of C_{18} (6 mL containing 500 mg of octadecylsilica) from Merck (Darmstadt, Germany) and PLRP-s (10 mm × 2 mm i.d. disposable precolumns containing 20 mg of polymeric material) from Spark Holland (The Netherlands).

Solid-phase extraction

(a) On-line SPE/LC/DAD

Preconcentration of the water samples, collected from the photodegradation reactor, was performed with an automated solid phase extraction (SPE) system

(Prospekt, Spark Holland, The Netherlands) coupled on-line with a liquid chromatograph. The SPE system consists of a cartridge exchange module, a solvent delivery unit (SDU), and a low-pressure six-port valve, which is connected directly to the gradient pumps of the HPLC system. Water samples were preconcentrated on PLRP-s polymeric cartridges. The cartridges were conditioned sequentially with 6 mL acetonitrile and 4 mL LC-grade water. Afterwards, a 24 mL aliquot of water sample was percolated through the cartridge at a flow-rate of 2 mL/min. Finally, the compounds trapped on the sorbent were eluted with the chromatographic mobile phase by switching the valve into the elute position.

LC-DAD analysis were performed with a Waters 600-MS solvent delivery unit with a 20 µL injection loop and a Waters 996 photodiode array detector (Waters, Millipore, MA). The analytical column used was a 25 cm × 4.6 mm i.d. packed with 5 µm of octylsilica gel from Shandon (Cheshire, England). The gradient elution was performed as follows: from 30% A (acetonitrile) and 70% B (HPLC water) to 100% A and 0% B in 25 min. Quantification was carried out with UV detection at 230 nm for Irgarol and at 250 nm for Diuron.

(b) Off-line SPE

An automated sample preparation system, ASPEC-XL, was used for the off-line preconcentration of water samples that were further analyzed by GC/MS. The ASPEC-XL system fitted with an external 306 LC pump for the dispensing of samples through the SPE cartridges and with a 817 switching valve for the selection of samples, was a gift from Gilson (Villiers-le-Bel, France). Water samples were preconcentrated on C_{18} cartridges. The first step of the solid-phase extraction consisted of conditioning the cartridge with 7 mL of ethyl acetate, 7 mL of methanol and 7 mL of LC-grade water at 1 mL/min. Afterwards, 160–900 mL of the water samples were percolated through the cartridge at 5 mL/min. The elution was carried out with 9 mL of ethyl acetate at 1 mL/min. The final extracts containing the compounds under study were evaporated with a stream of nitrogen up to 500 µL. Finally a volume of 1 µL was injected into the GC-MS system.

Mass spectrometric analysis

(a) LC-ESI/MS

Liquid chromatography/high flow pneumatically assisted electrospray/mass spectrometry, in positive ion mode of operation, was used for the identification of Irgarol byproducts. The eluent was delivered by a liquid chromatograph model HP 1090 (Hewlett-Packard, California). The mobile phases used for the elution of the analytes consisted of acetonitrile and water (0.01 M ammonium acetate) at a flow-rate of 0.8 mL/min. The gradient elution and the analytical column were the same as those used in the LC-DAD analysis. This HPLC system was connected to a HP mass spectrometer, model HP 1100, system equipped with an ESI probe. The different operating parameters included a drying gas (N_2) flow rate of 12 L/min and a nebulizer pressure of 40 psi, a capillary voltage of 3000 V and a fragmentor voltage of 70 V. The drying gas temperature was set at 350°C. Chromatograms were recorded under selected ion monitoring (SIM) and full SCAN (from m/z = 120 to 300) conditions.

(b) GC/MS

A Fisons (Manchester, England) MD 800 mass spectrometer coupled to a Fisons GC 8000 apparatus was used for GC-MS analysis in the electron impact (EI) mode. EI spectra was obtained at 70 eV, in full scan mode from *m/z* 50 to 300. A HP-5MS chromatographic column (30 m × 0.25 mm i.d., 5% of methyl phenyl siloxan) was from Hewlett Packard. The column was programmed from 60 to 280°C; 60°C was held for 1 minute and 300°C was held for 10 minutes. Injector temperature was set at 270°C, ion source temperature at 200°C, and transfer line at 280°C. Helium was used as the carrier gas with a head column pressure of 12 psi. (1 psi = 6894.76 Pa). The injection mode was splitless and the injection volume was of 1.0 µL.

Photodegradation studies

(a) Photolysis experiments

Water samples, spiked with a known amount of Irgarol, were placed in a quartz reservoir of 500 mL. Irradiations were carried out using a Suntest apparatus from Heraus (Hanau, Germany) equipped with a xenon arc lamp, as reported previously [7]. A second experiment was carried out with natural sunlight irradiation, using a capped quartz reservoir placed on a terrace roof at our institute in Barcelona, during September 1998. For the kinetic degradation study, the concentration of Irgarol in water was of 30 µg/L, and for the experiments of identification of byproducts by MS, Irgarol was spiked at 100 µg/L in order to be able to detect the lowest concentrations of byproducts as possible. Water samples were collected from the quartz reservoir at different periods of time, extracted on SPE cartridges and further analyzed by chromatographic techniques.

(b) Photosensitized degradations

These degradation experiments were carried out in the presence of photosensitizers, such as Fe^{3+} and TiO_2. The irradiations were carried out using the Suntest apparatus. Either TiO_2 or $FeCl_3$ were added to the 500 mL water sample at concentrations of 15 mg/L (as Fe^{3+}) and 10 mg/L (as TiO_2). Afterwards, the mixture was homogenized during 15 minutes by careful agitation followed by the addition of a known amount of Irgarol standard solution. Finally H_2O_2 at 0.05% (v/v) was added to the water sample. The same SPE methodology as that used in the photolysis degradations study was used for these experiments.

Calculation of half-life time

The calculation of half-life time [24] was performed using the first-order rate equation:

$$C_t = C_o e^{-kt} \tag{1}$$

where C_t represents the concentration at time t; C_0represents the initial concentration; and k is the rate constant (slope). When the concentration is reduced to 50% of its initial amount, half-life ($t_{1/2}$) can be determined by:

$$t_{1/2} = 0.693/k \tag{2}$$

where k is the degradation constant.

RESULTS AND DISCUSSION

Controlled photodegradation experiments

(a) Artificial light

The photodegradation kinetics study using a xenon lamp was carried out in different water matrices -deionized water, groundwater and seawater-spiked at 30 µg/L with Irgarol. A xenon arc lamp was used for the degradation studies due to the fact that results from photodegradation using natural sunlight are not reproducible. Moreover, xenon arc lamp has a similar spectral radiation to solar radiation showing a greater intensity [25, 26]. In this sense, aliquots of water sample were collected at different times after UV irradiation and analyzed by the on-line SPE-LC-DAD methodology. Figure la shows the percentage of degradation of Irgarol versus time of irradiation. No significant differences were observed in the three types of water samples, indicating that the degradation of Irgarol is not dependent on the type of matrix of water. In order to calculate the order of reaction, the log of Irgarol residual concentration was plot versus reaction time (see Figure 1b) and it was adjusted to a straight line. The rate constant k and half-life times $t_{1/2}$ were calculated from linear regression curves; the correlation coeffi-

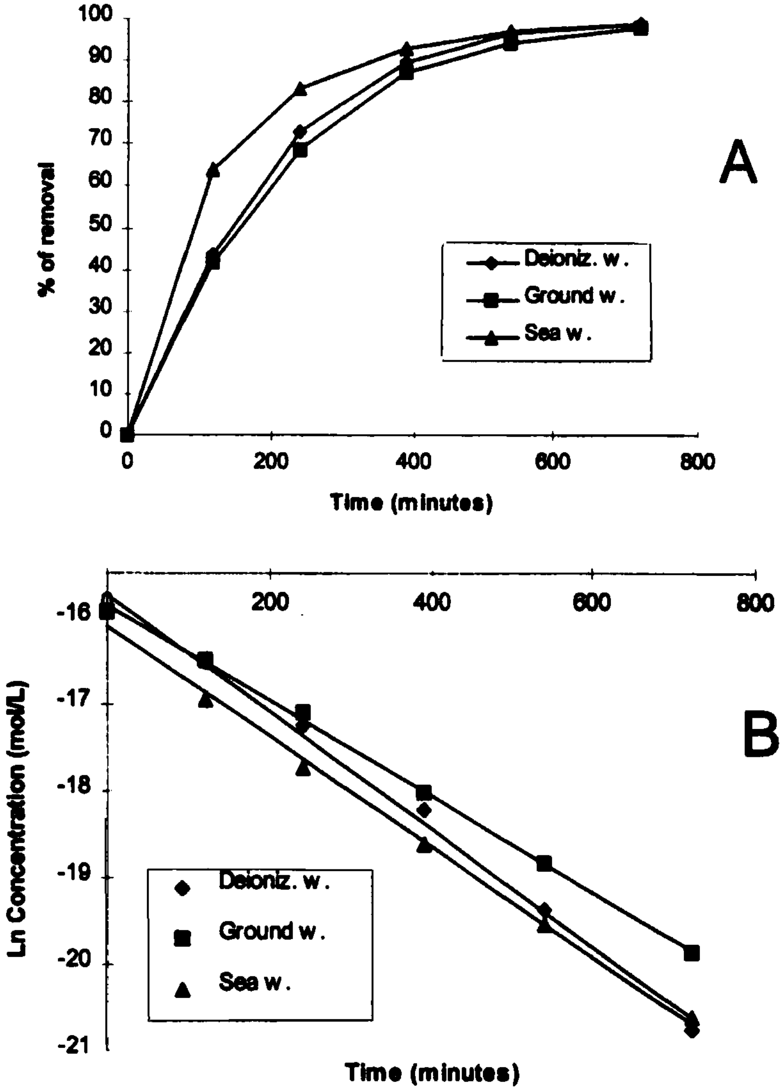

FIGURE 1 a) percentage (%) of Irgarol removal during photolysis in deionized, groundwater and seawater, using a Suntest lamp (n = 2). b) plot of log of Irgarol concentration Vs reaction time. Initial concentration of Irgarol: 30 μg/L

cients were around 0.99 and consequently both parameters can be considered as representative values. In Table I the results of the kinetics degradation study are summarized. A first reaction order kinetics was obtained for all types of water sample.

TABLE I Photodegradation kinetics of Irgarol using a xenon lamp. Experiments were carried out by on-line SPE-LC-DAD using C_{18} cartridges. Spiking level of Irgarol in water samples: 30 µg/L

	Reaction order	*Rate constant (min^{-1})*	*$t_{1/2}$ (minutes)*
Photolysis, deionized water	1	0.00668	103.8
Photolysis, ground water	1	0.00553	125.4
Photolysis, sea water	1	0.00645	107.5
Photodegradation with Fe^{3+}/H_2O_2	1	0.03247	21.3
Photodegradation with TiO_2/H_2O_2	1	0.04790	14.5

Due to the fact that chemical structures of Irgarol and atrazine are similar, the photodegradation kinetics of both compounds was compared. Table II shows the results obtained in a photodegradation study of atrazine [27] carried out under similar conditions to those used in this work. These results show the higher stability of Irgarol compared to atrazine, due to the presence of the tert-butyl and cyclopropyl group in the chemical structure. Atrazine, with much less stability, is an ubiquitous contaminant routinely determined, thus, it is expected that, if the use of Irgarol is continuously increased, its long-term monitoring will be needed.

TABLE II Photodegradation kinetics of atrazine in water under different conditions. Experiments were carried out by GC-NPD using C_{18} disks. Spiking level of atrazine in water samples: 36 µg/L [27]

Photodegradation	*Reaction order*	*Rate constant (min^{-1})*	*$t_{1/2}$ (minutes)*
Xenon lamp, deionized water	1	0.0177	39
Xenon lamp, ground water	s-1	0.0214	32
Xenon lamp, deionized water, Fe^{3+}/H_2O_2	1	0.1504	5
Sunlight, deionized water, Fe^{3+}/H_2O_2	1	0.0624	11
Xenon lamp, deionized water, TiO_2/H_2O_2	1	0.0336	21

s-1: pseudo-first order.
k: rate constant of degradation.

The photodegradation kinetics study was carried out in a quartz reservoir, which permits the adequate transmission of the radiation used in the experiments with the xenon lamp (>290 nm). Photodegradation experiments in Pyrex and Duran glass reservoirs were also performed as it is shown in Table III. In both cases the degradation of Irgarol and atrazine were very slow as compared with those obtained using quartz reservoirs. This indicates the required transmission of high wavelength radiation for the degradation of organic compounds in the environment. For this reason all the experiments carried out in this work were performed with a quartz reservoir instead of conventional glass materials.

TABLE III Photodegradation of Irgarol and atrazine using Pyrex, Duran and Quartz reservoirs and a xenon lamp. Experiments were carried out by on-line SPE-LC-DAD using C_{18} cartridges. Spiking level of Irgarol and atrazine in deionized water samples were 30 μg/L and 36 μg/L

	Pyrex		*Duran*		*Quartz*	
	0 hr.	*12 hr.*	*0 hr.*	*20 hr.*	*0 hr.*	*4 hr.*
Atrazine degradation (%)	0	24	0	45	0	98
Irgarol degradation (%)	0	11	0	32	0	73

(b) Natural sunlight

Since Irgarol has been detected in the Mediterranean coastal waters, the photodegradation study of Irgarol was also performed in natural seawater samples. In this sense, a quartz reservoir containing 500 mL of a seawater sample spiked at 30 μg/L with Irgarol was placed in a terrace roof during several days, in September of 1998. Sunlight hours were carefully recorded to assess the degradation of Irgarol as a function of solar hours. In this way, 75% and 98% of degradation was observed for Irgarol after 96 and 217 hours of solar irradiation, respectively. These degradation percentages would be much lower with longer half-life time, in autumn and winter, than in summer time like in September. For instance, Zepp and Cline [28] found that half-life time of carbaryl increased 8 times in December as compared to September. It is important to take into account that under real conditions, Irgarol can be degraded in water by other processes such as biodegradation and hydrolysis, and it can be removed by evaporation and sedimentation.

Degradation products

The photolysis and photodegradation studies carried out for Irgarol allowed us to identify, for the first time, four new byproducts by means of mass spectrometric techniques. The byproducts: 2-*tert*-butylamino-*s*-triazine (1), 2-methylthio-4-cyclopropylamino-*s*-triazine (2), 2-*tert*-butylamino-4-cyclopropyl-amino- *s*-triazine (3) and 2-methylthio-4-*tert*-butylamino-*s*-triazine (4) were identified by GC-MS(EI) and LC-ESI/MS. Figure 2 shows GC-MS traces extracts of two groundwater samples, collected after 7 and 10 hours of xenon lamp irradiation. Byproduct 2 was detected at low concentration in the experiments of photolysis in ground water. Figure 3 shows the GC-MS spectra of the

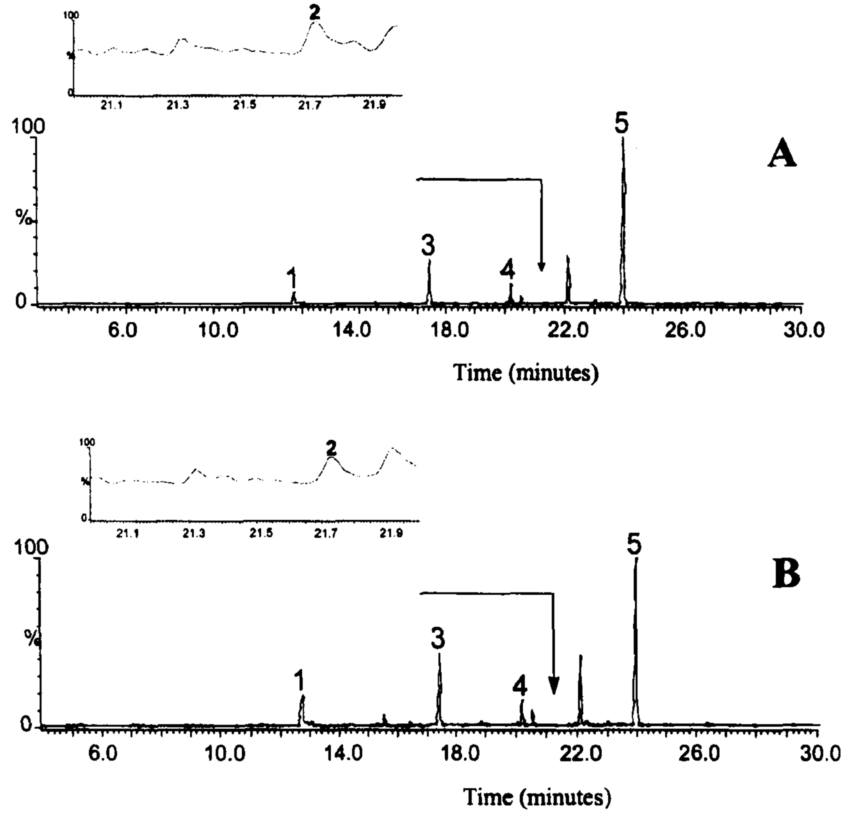

FIGURE 2 GC-MS chromatograms, in Full Scan, of extracts corresponding to two samples removed during the photolysis of Irgarol in groundwater. a) after 7 hours of irradiation with a xenon lamp, and b) after 10 hours of irradiation. Peak numbers: (1) 2-*tert*-butylamino-*s*-triazine, (2) 2-methylthio-4-cyclopropylamino-*s*-triazine, (3) 2-*tert*-butylamino-4-cyclopropyl-amino-*s*-triazine, (4) 2-methylthio-4-*tert*-butylamino-*s*-triazine and (5) Irgarol

four byproducts, which present as molecular ion 167 {27%} (compound 1), 197 {71%} (compound 2), 207 (compound 3) {49%} and 213 (compound 4) {46%}.

Degradation product 1 exhibited fragment ion peaks at *m/z* 152 (M^+-CH_3) {base peak, 100%}, 111 (M^+-*tert*-butyl) {57%} and 83 (M^+-*tert*-butyl-N_2) {23%}. Degradation product 2 exhibited fragment ion peaks at *m/z* 182 (M^+-CH_3) {base peak, 100%}, 150 (M^+-SCH_3) {7%} and 109 (M^+-cyclopropyl-SCH_3) {37%}. Degradation product 3 exhibited fragment ion peaks at *m/z* 192 (M^+-CH_3) {41%}, 150 (M^+-*tert*-butyl) {52%} and 136 (M^+-*tert*-butyl-N) {base peak, 100%}. Degradation product 4 exhibited fragment ion peaks at *m/z* 198 (M^+-CH_3) {peak base, 100%}, 157 (M^+-*tert*-butyl) {87%}, 111 (M^+-*tert*-butyl-SCH_3) {21%} and 83 (M^+-*tert*-butyl-SCH_3-N_2) {23%}.

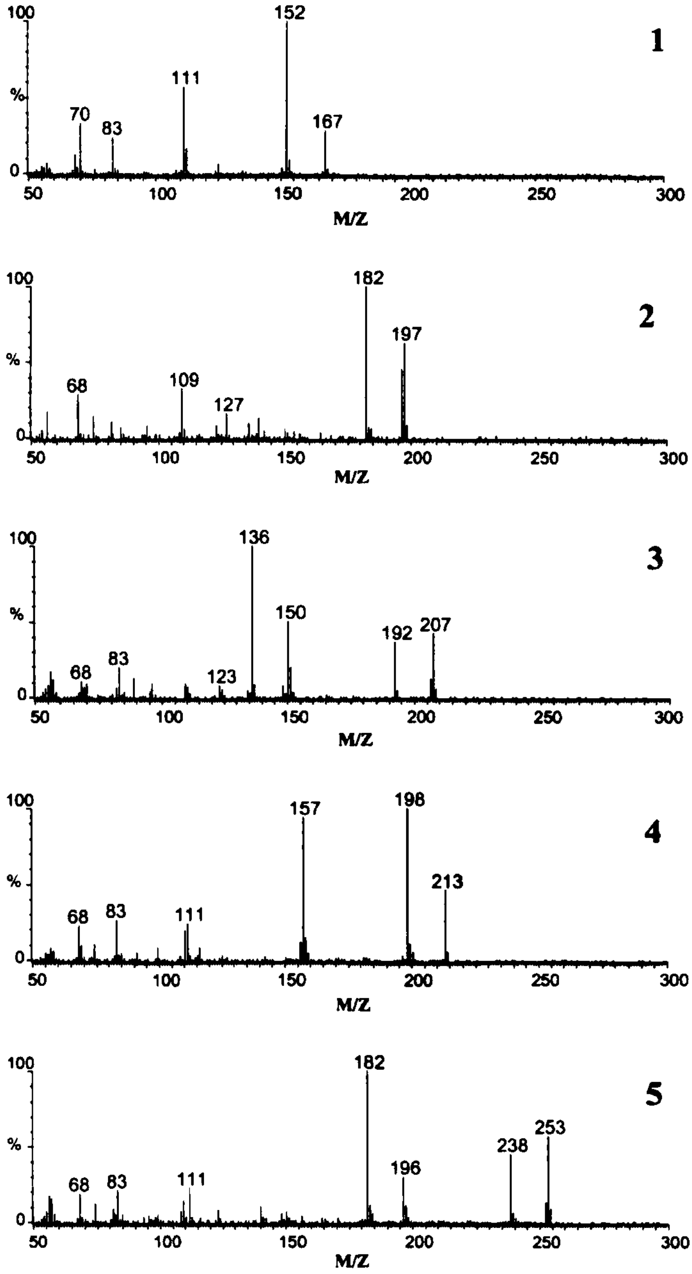

FIGURE 3 GC-MS spectra of byproducts detected in the photolysis of Irgarol in groundwater corresponding to the chromatogram from Figure 2

The same byproducts as those identified by GC-MS were confirmed also by LC-ESI/MS Table IV shows the fragment ions at two fragmentor voltages, 70 V and 120 V. Figure 4 shows the chromatogram obtained of a sea water sample, irradiated during 7 hours with a xenon lamp, after its analysis by on-line SPE-LC-ESI/MS. The presence of the four byproducts was unequivocally confirmed by this technique.

TABLE IV Typical fragment ions and relative abundances (%) of byproducts by LC-ESI/MS in positive mode of operation. Fragmentor voltage set at 70 V and 120 V

Byproduct	*Fragment ion at 70 V* $[M + H]^+$	*Fragment ion at 120 V*
1	168	112 {100%}; 168 {20%}
2	198	198 {100%}
3	208	152 {100%}; 208 {25%}
4	214	158 {100%}; 214 {20%}

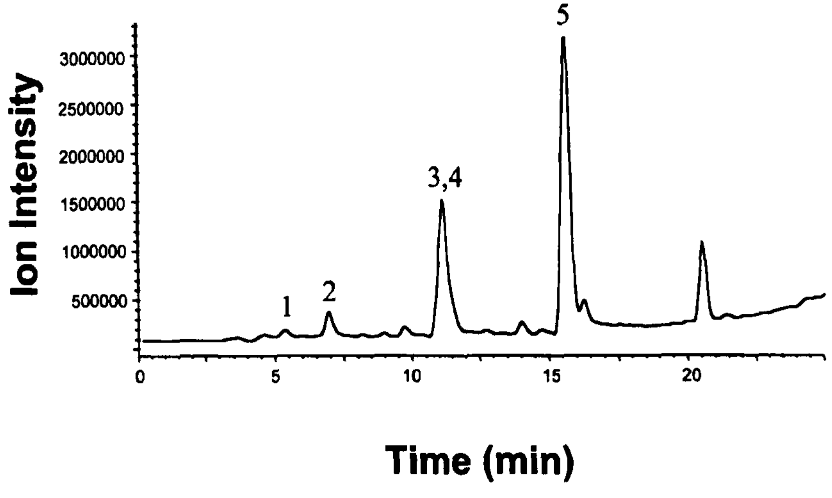

FIGURE 4 Chromatographic traces of a seawater sample, irradiated during 7 hours with a xenon lamp, after its analysis by on-line SPE-LC-ESI/MS under SCAN conditions. Peak numbers: (1) 2-*tert*-butylamino-*s*-triazine, (2) 2-methylthio-4-cyclopropylamino-*s*-triazine, (3) 2-*tert*-butylamino-4-cyclopropyl-amino-*s*-triazine, (4) 2-methylthio-4-*tert*-butylamino-*s*-triazine and (5) Irgarol

Table V shows the relative percentage concentrations of four byproducts in samples removed during the laboratory photolysis photodegradation study, as well as that carried out irradiating with natural sunlight. The degradation product 4 was the only byproduct formed in the latter case. The presence of this byproduct in the spiked seawater samples was totally confirmed by identical match of retention time and spectrum of a standard. Byproduct 4 has also been detected in other degradation experiments, such as in a biodegradation study of Irgarol by *Phanerochaete chrysosporium* carried out by Liu et al. [6]. This byproduct is formed from Irgarol by losing easily the cyclopropyl group both in photodegradation and biodegradation processes. Figure 5 shows photodegradation pathways of Irgarol in water.

TABLE V Relative concentration percentage (%) of Irgarol and its four byproducts in water samples collected from the photodegradation experiments. Analysis were carried out by GC-MS (EI). Initial concentration of Irgarol was of 100 μg/L

Sample	*Met. 1 (12.75)*[a]	*Met. 2 (21.74)*	*Met. 3 (17.44)*	*Met. 4 (20.19)*	*Irgarol*[b] *(24.00)*
Photolysis in deionized water, 0 hr.					100.00
Photolysis in deionized water, 4 hr.			9.89	3.87	73.95
Photolysis in deionized water, 10 hr.	3.82		13.41	1.16	23.30
Photolysis in ground water, 0 hr.					100.00
Photolysis in ground water, 4 hr.	0.86		8.03	3.30	53.65
Photolysis in ground water, 7 hr.	3.58	0.20	13.00	3.98	51.30
Photolysis in ground water, 10 hr.	4.21	0.20	7.29	1.54	27.88
Photolysis in sea water, 0 hr.					100.00
Photolysis in sea water, 4 hr.	0.66		7.63	2.69	53.82
Photolysis in sea water, 7 hr.	3.37		14.54	2.43	45.63
Photolysis in sea water, 10 hr.	3.24		9.94	1.26	34.23
Photodegradation with TiO_2, 0 hr					100.00
Photodegradation with TiO_2, 1 hr.		1.36	1.13	13.30	48.68
Photodegradation with TiO_2, 2 hr.	1.70	1.85	1.49	10.88	19.66
Photodegradation with TiO_2, 3 hr. 15 min.	0.73	1.04	0.36	1.57	4.88
Photodegradation with $FeCl_3$, 0 min.					100.00
Photodegradation with $FeCl_3$, 30 min.		0.27		7.88	35.47
Photodegradation with $FeCl_3$, 75 min.		0.23	1.28	6.42	7.02
Photodegradation with $FeCl_3$, 150 min.			0.13	0.82	0.65
Photolysis with sunlight, sea water, 0 hr.[c]					100.00
Photolysis with sunlight, sea water, 96 hr.[c]				30.11	25.36
Photolysis with sunlight, sea water, 217 hr.[c]				24.09	2.01

a. Retention time indicated in parenthesis.

b. % of Irgarol degradation.

c. Photodegradation carried out with sunlight, the others with xenon lamp blanks: not found.

To our knowledge this is the first time that a photodegradation study for Irgarol is carried out in natural seawater samples. Studies of photodegradation are important in order to understand the fate of new organic compounds released into the environment. Not only the presence of the target compound is an important issue of knowledge but also that of possible byproducts, which can even, be more toxic and persistent than the parent compounds.

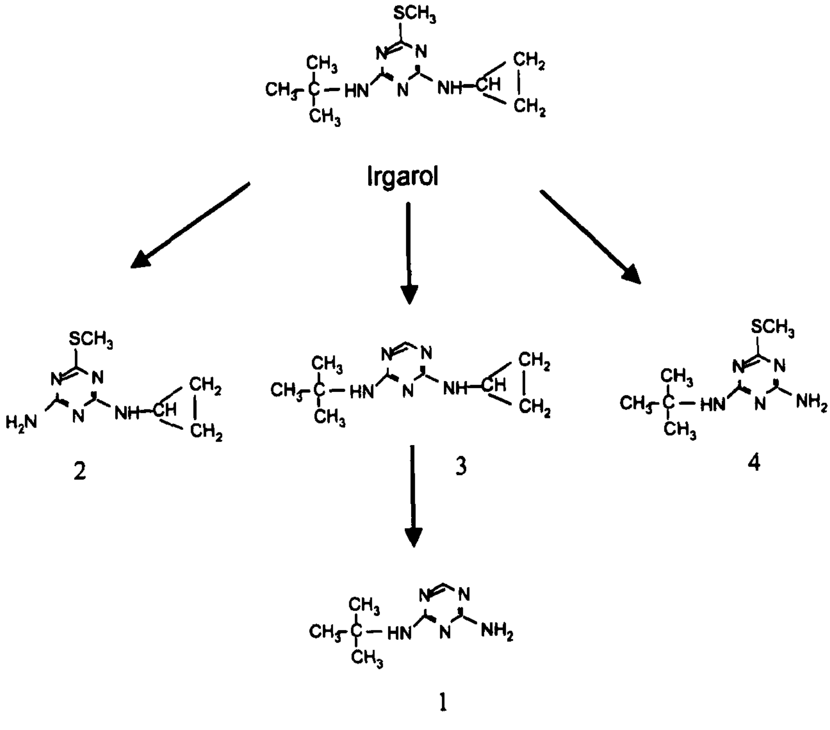

FIGURE 5 Photodegradation pathway of Irgarol in water. Compound numbers correspond to peak numbers of Figures 2 and 4

Decontamination of polluted waters

Contamination of water by xenobiotic compounds such as Irgarol presents a serious environmental problem because of their potential toxicity. Thus, their removal from the aquatic environment has become a very important issue, and for this purpose different physical and chemical methods are used, namely carbon adsorption, ozonation, microbial or photodegradation. Hydrolysis, photolysis, aquatic metabolism and field dissipation can also contribute to decomposition [29]. Photodegradation of contaminants with sunlight may be slow because several xenobiotics are photostable and, moreover, solar radiation may vary with the season and the meteorological conditions. [30]. For this reason, the photodegradation of xenobiotic compounds is assisted by inorganic semi-conductors such as TiO_2 [31, 32] or photosensitized by iron (III) [33, 34]. Photosensitized degradation using H_2O_2 is also accelerated [35], by the rapid formation of hydroxyl free radical.

In the previous section it has been demonstrated that radiation above 290 nm is required for Irgarol degradation, so that, in case of increasing its use, it could be accumulated in seawater. In some places with lack of surface water, seawater is being depurated for domestic use. For this reason, the development of different methods for the removal of contaminants from water is necessary. The removal of xenobiotics by photosensitized degradation has been the main objective of previous works [8–11, 27, 30].

In Table I the results obtained with the use of Fe^{3+} or TiO_2, as sensitizers, are reported, showing a faster photodegradation of Irgarol when these reagents are present in the water sample. The sensitizers decompose hydrogen peroxide and water forming hydroxyl free radicals which oxide Irgarol. Hydroxyl free radical is a strong oxidant agent and in this way Irgarol is rapidly oxidized. Fast photodegradation with these kind of sensitizers has also been obtained in previous photodegradation studies, such as those reported with alachlor [8], chlorpyrifos [9], endosulfan [10], chlorothalonil [11] and atrazine [27].

Table V shows the relative percentage concentration of four byproducts in samples removed during the sensitized photodegradation. In the photodegradation with Fe^{3+}, Irgarol was degraded quite rapidly. Moreover, byproducts were formed in low amounts and byproduct 4 was also degraded, indicating that photosensitized degradation either with Fe^{3+}or TiO_2 can be used for decontamination of polluted waters.

Overall, the present study reported four new byproducts of Irgarol formed under photolysis and sensitized photodegradation conditions. These byproducts were 2-*tert*-butylamino-*s*-triazine (1), 2-methylthio-4-cyclopropylamino-*s*-triazine (2), 2-*tert*-butylamino-4-cyclopropyl-amino-*s*-triazine (3) and 2-methylthio-4-*tert*-butylamino-*s*-triazine (4). The byproduct 4 was formed in a photodegradation experiment of Irgarol in seawater, using solar radiation.

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