

Photochemical degradation study of irgarol 1051 in natural waters: influence of humic and fulvic substances on the reaction

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Abstract

The photochemical degradation of irgarol 1051 has been studied in different natural waters (sea, river, lake) as well as in distilled water under natural and simulated solar irradiation. The effect of dissolved organic matter (DOM) such as humic and fulvic substances on the photodegradation rate was also studied under simulated sunlight. The addition of DOM in distilled water was shown to greatly increase the rate of degradation, however, a decrease was observed in natural waters. The photodegradation proceeds via pseudo-first-order reaction in all cases with half-lives ranged from 2 to 1432 h. In natural and humic water irgarol 1051 photodegradation gave rise to the dealkylated derivative demonstrating that the transformation of irgarol 1051 depend on the constitution of the irradiated media and especially from DOM concentration and type. The byproducts identified by GC–MS techniques were: 2-methylsulfonyl-4-terbutylamino-6-cyclopropylamino-*s*-triazine, 2-hydroxy-4-terbutylamino-6-cyclopropylamino-*s*-triazine, 2-methylthio-4-terbutylamino-6-ethylamino-*s*-triazine, 2-methylsulfonyl-4-terbutylamino-6-amino-*s*-triazine and diaminohydroxy-*s*-triazine. © 2002 Published by Elsevier Science B.V.

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1. Introduction

Irgarol 1051 (2-methylthio-4-terbutylamino-6-cyclopropylamino-*s*-triazine) is a newly developed herbicide which in the last few years has been used as an alternative to TBT biocide agent in antifouling paints [1]. These paints are applied to the hulls of ships and boats to prevent the growth of bacteria, macroalgae, mussels and other invertebrates. Irgarol 1051 like other biocides is slowly released over a period of time in the aquatic environment and important coastal concentrations have been found in areas of high yachting activity and sportive harbors [2–4]. It is, therefore, needed to collect data on this molecule for a better knowledge of its fate in natural waters and for the risk assessment.

The study of the photochemical behavior of a contaminant is a key issue in environmental studies in order to assess its degradation and the formation of toxic transformation products. The fate and degradation of organic micropollutants are largely affected by the presence of organic matter like humic and fulvic substances widespread in water–soil environment systems, that strongly absorb light leading to the formation of reactive oxygen intermediates [5]. Dissolved organic matter (DOM) can either enhance [6] or inhibit the rate of photolysis [7].

Irgarol 1051 does not appear to undergo rapid biodegradation while only a few studies have been recently reported describing irgarol photodegradation where the formation of 2-methylthio-4-terbutylamino-6-amino-*s*-triazine has been observed as the main transformation byproduct [8]. The environmental detection of this compound in seawater samples has been also reported [9,10]. However, the fate and transformation pathways of irgarol 1051 in the aquatic environment are not yet fully understood.

This paper examines the kinetic and mechanistic aspects of the photochemical transformation of irgarol 1051 under a variety of reaction conditions. The phototransformation of this molecule was studied in distilled and natural waters in order to obtain basic data on the photoreactivity and on the nature of photoproducts as well as to predict its environmental fate in the aquatic environment. In addition, we examined the influence of humic and fulvic substances (DOM) on the degradation as well as the photodecomposition reaction products which were evaluated.

2. Experimental

2.1. Water samples and chemicals

Irgarol 1015 was purchased from Riedel-de Hën (Germany). Humic acid (HA) and fulvic acid (FA)

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Table 1
Characteristics of selected environmental waters

Water type	pH	Conductivity ($\mu\text{S}/\text{cm}$)	TDS ^a	TOC ^b (mg/l)	Salinity (%)
Distilled	5.72	1.1	n.d. ^c	b.d.l. ^d	n.d.
Ionian sea	7.72	52.800	219	2.53	3.65
Kalamas river	7.90	318	198	5.11	1.7
Pamvotis lake	7.67	326	358	10.34	0.51

^a Total dissolved solids.

^b Total organic carbon.

^c Not determined.

^d Below detection limit.

(isolated from Suwannee River) standards were purchased from Fluka and International Humic Substances Society (IHSS), respectively. Pesticide grade *n*-hexane, dichloromethane and ethylacetate were purchased from Pestiscan (Labscan, Dublin, Ireland). Sodium sulfate (pro-analysis) was from Merck (Darmstadt, Germany). Styrenedivinylbenzene (SDB) extraction disks (47 mm) were purchased from 3 M Empore (St. Paul, USA). Concentration of total organic carbon (TOC) in the natural water samples was measured on a total carbon analyzer (TOC-5000 Shimadzu) using the high temperature catalytic oxidation method (HTCO) and were as follows: sea water (2.53 mg/l), river water (5.11 mg/l), lake water (10.34 mg/l). All water samples were used without previous treatment, filtration or sterilization. The water samples were analyzed to ensure that they were free of interfering compounds. Their physicochemical characteristics are given in Table 1.

2.2. Irradiation procedure

Photodegradation rates of irgarol 1051 were determined in natural waters (sea, river and lake) and in distilled water under natural and simulated solar irradiation. Samples containing 1 mg/l irgarol 1051 were all exposed to solar light in capped Pyrex glass reservoirs placed at the University Campus (roof terrace of the Department of Chemistry), during the period May–June 2000. Three samples were employed for each water.

Incident solar radiation (W/m^2) was measured with a radiometer (Eppley Lab., Newport, RI) in the wavelength range of 285–2800 nm. The mean sunlight intensity at the beginning, middle and end of the day was estimated, respectively, as 231, 651 and 278 W/m^2 during May and 252, 715, and 322 W/m^2 during June 2000. The average total daily short-wave radiation for this period was 682 W/m^2 , with a 10 h mean sunshine duration from sunrise to sunset. The mean daily temperature was 21.1 °C and maximum and minimum air temperatures were 36.2 and 7.8, respectively.

Artificial light for the laboratory experiments was provided by a Suntest CPS + apparatus from Heraeus (Hanau,

Germany), equipped with a xenon arc lamp (1500 W) and special glass filters restricting the transmission of wavelength below 290 nm. The aqueous solutions (50 ml) of irgarol 1051 were exposed to simulated solar irradiation in a 6.5 cm diameter cylindrical Duran glass UV-reactor. The light source was on the top of the reactor and an average irradiation intensity of 750 W/m^2 was maintained throughout the experiments measured by internal radiometer. The temperature of samples did not exceed 25 °C using tap water cooling circuit for the UV-reactor. In all cases dark controls were run at the same concentration and conditions as those of the corresponding photodegradation in natural and simulated sunlight.

The effect of DOM was examined in distilled water in the presence of various concentrations of HA and FA ranged from 4 to 24 mg/l. Irradiations were carried out using the suntest apparatus, the same reactor and initial concentration of irgarol 1051.

2.3. Sample analysis

For the determination of the kinetic rate constants liquid–liquid extraction was chosen as it is a simple and reliable method for quantification of pesticides in water especially when using low extraction volumes.

At specific time intervals samples of 5 ml were withdrawn from the Pyrex glass reservoirs and the UV-reactor. The samples were extracted twice with 2.5 ml *n*-hexane for 1 min using a vortex, dried with a small amount of Na_2SO_4 and finally analyzed by GC, quantified by internal standard.

For the identification of the transformation products, the left solutions (700 ml) of the outdoor experiments and 50 ml of aqueous solutions irradiated under simulated solar light were extracted by means of solid phase extraction using SDB extraction disks, as described previously by our group [11].

Photodegradation kinetics were performed using a Shimadzu 14 A gas chromatograph equipped with flame thermionic detector (FTD) at 250 °C. A DB-5 column (30 m \times 0.32 mm ID) was programmed from 150 (held for 2 min) to 210 °C at a rate of 5 °C/min (held for 14 min) and to 270 °C at a rate of 20 °C/min. Injector temperature was set to 240 °C. Helium was used as the carrier gas. The detector gases were hydrogen and air and the ion source of FTD was an alkali metallic salt (Rb_2SO_4) bonded to a 0.2 mm spiral of platinum wire.

A GC–MS, QP 5000 Shimadzu instrument equipped with a DB-5-MS column (30 \times 0.25 mm ID) was used for the identification of the transformation products under the following chromatographic conditions: injector temperature 250 °C, oven temperature program from 55 (held for 2 min) to 210 °C at a rate of 5 °C/min (held for 20 min) and to 270 °C at a rate of 10 °C/min. Helium was used as the carrier gas and 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.

3. Results and discussion

3.1. Photodegradation kinetics

First-order kinetic behavior was observed for the photodegradation of irgarol 1051 in all cases. The photodegradation constants were calculated by subtracting the exponents of different degradation curves representing the apparent degradation and the degradation owed to hydrolysis, volatilization and biodegradation (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. Quantitative recoveries from dark controls sampled over the entire exposure period of simulated solar irradiation showed that irgarol 1051 was very stable and did not degrade in environmental waters as well as in the aqueous solutions of HA and FA. The first-order rate constants (k_{phot}) and the half-lives ($t_{1/2}$) for natural and simulated solar irradiation are presented in Table 2.

The degradation curves (Figs. 1 and 2) demonstrate that photolysis of irgarol 1051 were lower in environmental waters compared to distilled water, showing a strong dependence on the constitution of the irradiated media and especially from the concentration of TOC. After 66 calendar days (1584 h) of daylight exposure 66, 60, 57 and 65% of irgarol 1051 was degraded in distilled, sea, river and lake water, respectively, while more than 66, 57, 55 and 53% degraded within 48 h under simulated solar irradiation. The rate constant data show that the presence of TOC in natural waters inhibits the degradation rate of irgarol 1051. The retarded photodegradation indicate that organic matter absorbed most of the photons emitted thereby slowing down direct photochemical reaction of irgarol 1051 (optical filter effect) [12]. Also particulate matter such as sediment particles and microorganisms suspended in the water column may scatter incident light, greatly reducing

Table 2

Kinetic parameters of direct and sensitized photolysis of irgarol 1051 in different aqueous media

Photolysis	$t_{1/2}$ (h)	k_{phot} (h^{-1})	R^2
<i>Natural solar irradiation (outdoor)</i>			
Distilled water	1118	0.00062	0.989
Sea water	1342	0.00052	0.989
River water	1432	0.00048	0.991
Lake water	1238	0.00056	0.994
<i>Simulated solar irradiation (suntest)</i>			
Distilled water	29	0.0236	0.998
Sea water	38	0.0182	0.992
River water	43	0.0163	0.993
Lake water	40	0.0172	0.987
<i>Simulated solar irradiation (suntest)^a</i>			
Humic, 4 mg/l	7	0.0953	0.999
Humic, 8 mg/l	6	0.1078	0.989
Humic, 16 mg/l	4	0.1550	0.991
Humic, 24 mg/l	2	0.3080	0.996
<i>Simulated solar irradiation (suntest)^a</i>			
Fulvic, 4 mg/l	9	0.0787	0.991
Fulvic, 8 mg/l	8	0.0879	0.994
Fulvic, 16 mg/l	6	0.1169	0.999
Fulvic, 24 mg/l	5	0.1443	0.996

^a Distilled water.

penetration of light beneath the surface. Photoreaction of the colored dissolved organic matter (CDOM) in sunlight caused a decrease mostly in the UV-B (280–315 nm) [13] region which is very important in the case of irgarol 1051 that does not absorb strongly above 320 nm (Fig. 3). Another, reason may be that irgarol 1051 was partially bound to DOM ($\log K_{\text{oc}} = 3.0$, $\log K_{\text{ow}} = 3.9$) 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 [14]. However, a sensitization

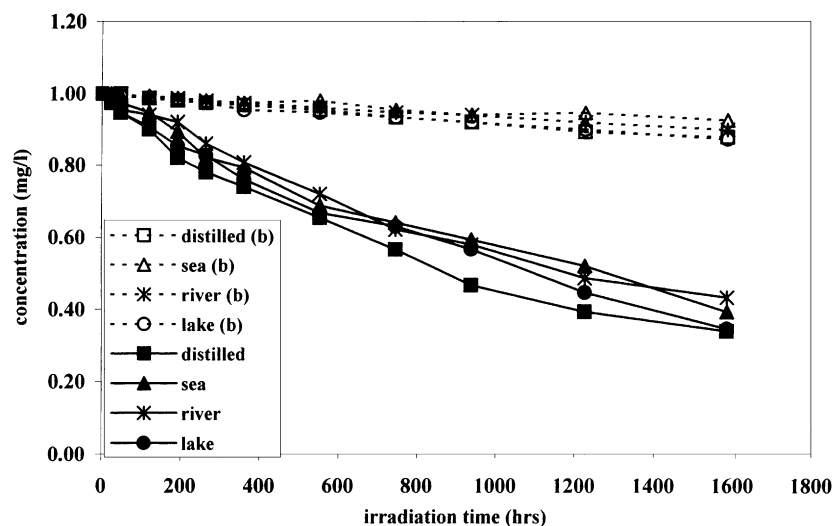


Fig. 1. Photodegradation of irgarol 1051 in natural and distilled water under natural solar irradiation ((b): blank experiment).

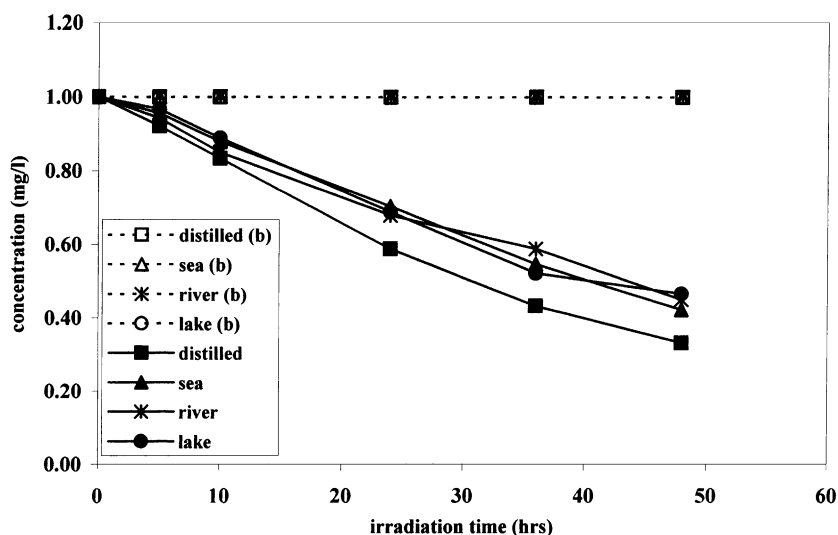


Fig. 2. Photodegradation of irgarol 1051 in natural and distilled water under simulated solar irradiation ((b): blank experiment).

effect of humic substances cannot be excluded. DOM and other reactive chromophores in natural water such as riboflavin and flavin absorb sunlight energy and are known to provide a rich variety of photochemical reactions initiating indirect photodegradation of organic contaminants [15]. Although, the identity of the sensitizers is unknown, dissolved HA and FA as well as inorganic ions like nitrate and nitrite have been shown to sensitize the photodegradation of organic contaminants in aqueous solutions [16].

This sensitization effect was examined by experiments that were carried out using the same initial concentration of irgarol 1051 and various concentrations of HA and FA in distilled water, under simulated solar irradiation. In the presence of HA and FA faster degradation of irgarol 1051 was observed as compared to direct photolysis in distilled water. Experiments conducted with concentration 4, 8, 16 and 24 mg/l of HA and FA in 24 h photoperiod resulted in 90, 92, 98 and 100% disappearance of irgarol 1051, respectively. The same tendency has been observed also in the case of FA where 85, 88, 94 and 97% degradation of irgarol 1051 was observed at concentrations of 4, 8, 16 and 24 mg/l, respectively. In addition no strong associates were

formed between irgarol 1051 and HA as indicated by our group [17] during the determination of binding coefficient using the SPME technique. Figs. 4 and 5 display the rate data for these experiments. HA have shown greater ability to sensitize the photolysis of irgarol 1051. Due to the lack of data relating to carbon, nitrogen and oxygen content of HA no comparison could be made concerning their structural characteristics. Photochemical properties of humic and fulvic substances result from complex phenomena and depend on many factors, the origin of each substance being the most important [18].

The photolysis was faster under simulated irradiation compared to natural sunlight. This observation seems normal when considering the sunlight intensity variation depending on the time of day and on cloud cover while the suntest apparatus keeps the intensity constant. In the case of suntest experiment, 48 h photoperiod was used in calculating rate constants while in the case of outdoor experiment real 24 h were used. By including the effects of diurnal cycling, the reported photolysis rates of the outdoor experiments will be substantial slower, however, this will also provide more realistic environmental transformation rates.

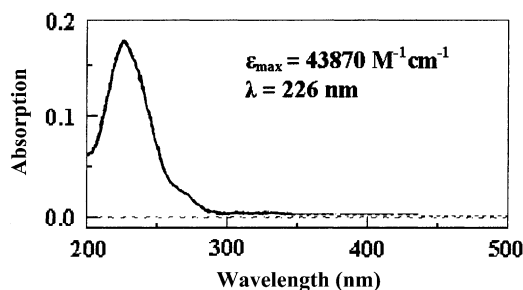


Fig. 3. Absorption spectrum of irgarol 1051 in distilled water (3.95×10^{-6} M).

3.2. Photodegradation products

Up to five compounds could be detected as possible degradation intermediates during the photodegradation of irgarol 1051 in the presence of humic and fulvic substances (DOM), while three compounds were identified during irgarol direct photolysis in distilled water. These compounds were identified by comparing with mass spectra previously published by our group [11]. A total ion chromatogram (TIC) obtained by GC–MS for an SPE extract of irgarol 1051 solution after 24 h of simulated solar irradiation in humic water (24 mg/l) is shown in Fig. 6.

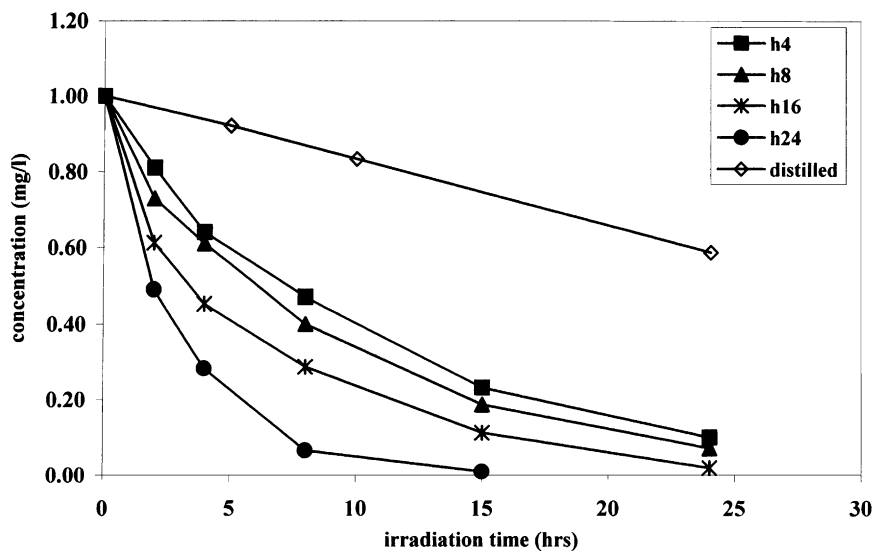


Fig. 4. Photodegradation of irgarol 1051 in various concentrations (4, 8, 16 and 24 mg/l) of HAs in distilled water under simulated solar irradiation (h4–h24: HA in concentration 4–24 mg/l, respectively).

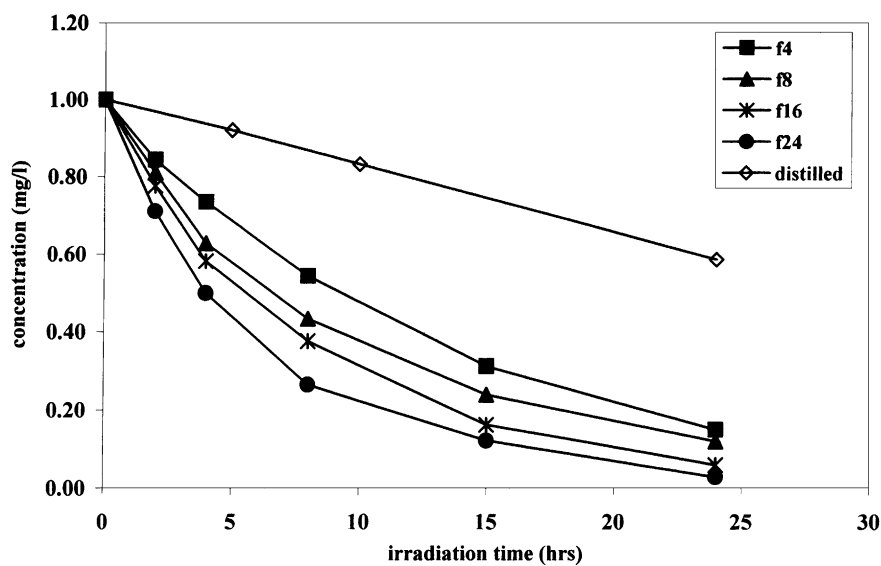


Fig. 5. Photodegradation of irgarol 1051 in various concentrations (4, 8, 16 and 24 mg/l) of FAs in distilled water under simulated solar irradiation (f4–f24: FA in concentration 4–24 mg/l, respectively).

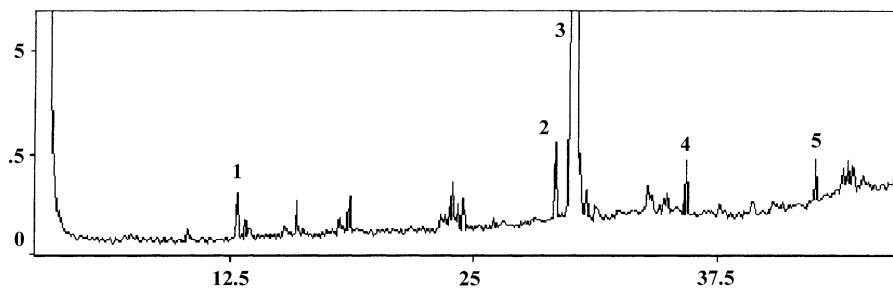


Fig. 6. TIC of irgarol 1051 photodegradation in distilled water in the presence of 24 mg/l of humic substances.

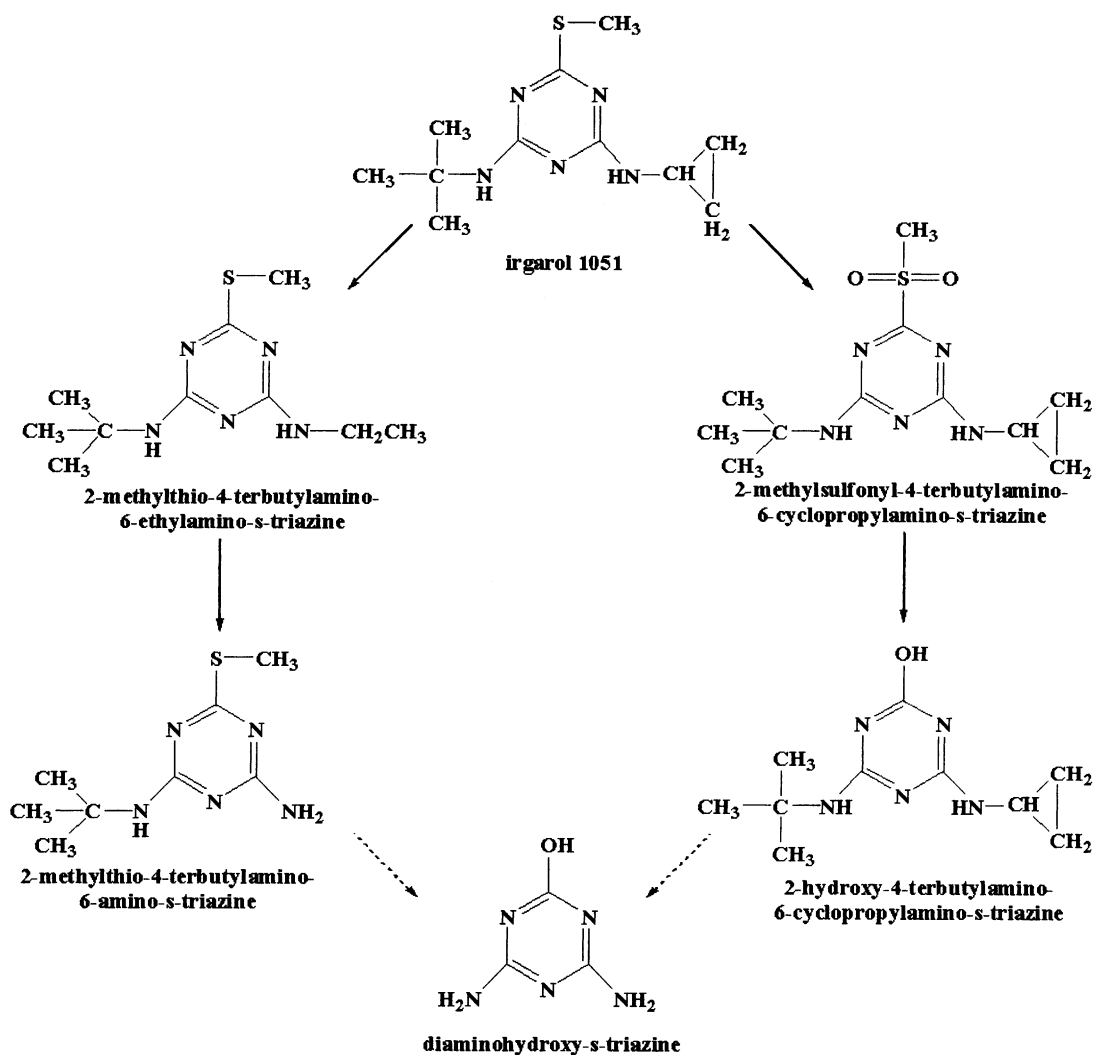


Fig. 7. Proposed photodegradation pathway of irgarol 1051 in natural waters.

Two routes of degradation pathways are observed during the photodegradation of irgarol 1051 in distilled water (direct photolysis) according to the proposed reaction scheme (Fig. 7). The first route involves the oxidation of irgarol's sulfur atom leading to the formation of sulfone (compound **5**, $t_R = 42.46$ min). The cleavage of the sulfur group of the triazine ring results in the formation of 2-hydroxy-4-terbutylamino-6-cyclopropylamino-s-triazine (compound **2**, $t_R = 29.24$ min). This observation is in agreement with other studies describing the direct photolysis of *s*-triazines where photoreaction must not involve the alkyl group but the methylthio or the chlorine group supporting that hydroxy derivative formation is a major pathway in direct photolysis [19–21]. Thus, the formation of the mono-dealkylated derivative, 2-methylthio-4-terbutylamino-6-amino-*s*-triazine (compound **3**, $t_R = 29.97$ min) that was greatly favored over the hydroxylated and the sulfonyl derivative since it occurred for more than 90% of photoreaction (according

to relative abundance of the compounds) was somewhat unexpected. Okamura et al. [8] has also reported the presence of this byproduct as the main during irgarol 1051 photolysis in distilled water, while Torrents et al. [19] has observed the formation of chlorodealkylated derivatives in the case of atrazine during direct photolysis. Irradiation of aqueous irgarol 1051 solutions containing DOM during simulated solar irradiation, resulted in the formation of diaminohydroxy-*s*-triazine (compound **1**, $t_R = 12.94$ min), indicating both an increase in photosensitization and in $\bullet\text{OH}$ processes. Singlet oxygen formed during the photolysis reacts with DOM to form peroxide. It is possible that the peroxide formed may generate the hydroxyl radicals from the humic solution, which in turn causes dealkylation [19]. 2-Methylthio-4-amino-6-ethylamino-*s*-triazine (compound **4**, $t_R = 35.85$ min) was also formed during these series of experiments apart from the derivatives mentioned in distilled water (compounds **2**, **3** and **5**) showing that in the presence of DOM both direct and indirect reactions can occur.

Table 3
Distribution of degradation products identified in aqueous solutions of irgarol 1051

	Degradation products					Irgarol
	1	2	3	4	5	
Distilled	–	+	+	–	+	+
Sea	+	–	+	–	+	+
River	+	+	+	–	–	+
Lake	+	+	+	–	+	+
Humic 4 ^a	+	+	+	–	–	+
Humic 8	+	+	+	+	+	+
Humic 16	+	+	+	–	+	+
Humic 24	+	+	+	+	+	–
Fulvic 4	+	–	+	–	+	+
Fulvic 8	+	+	+	+	+	+
Fulvic 16	+	+	+	+	+	+
Fulvic 24	+	+	+	+	+	+

^a Distilled water (mg/l).

The product profile of irgarol photodegradation in natural waters (Table 3) was very similar to that of HA/FA system, which strongly suggests that DOM present in natural waters sensitize the photolysis of irgarol 1051 as indicated by the formation of the dealkylated derivative, namely diaminohydroxy-*s*-triazine. However, in this case too, 2-methylthio-4-terbutylamino-6-amino-*s*-triazine was the main byproduct formed proving its occurrence in surface waters.

4. Conclusions

In the current study, the degradation rates of irgarol 1051 in natural waters were in general lower compared to distilled water, showing a strong dependence on the constitution of the irradiated media. Irradiation of aqueous irgarol 1051 solutions containing dissolved humic and fulvic substances under simulated solar irradiation had a significant influence on the degradation of the compound. The similar distribution pattern of the transformation products in natural waters and in distilled water in the presence of HA and FA suggests the sensitization effect of DOM in natural waters, that is however, hidden by the strong filter effect. DOM concentration and presumably the type of functional groups and aromaticity present in DOM will influence the photo-processes differently. The major transformation products identified using GC–MS techniques were the hydroxy and dealkylated derivatives, 2-methylsulfonyl-4-terbutylamino-

6-cyclopropylamino-*s*-triazine, 2-hydroxy-4-terbutylamino-6-cyclopropylamino-*s*-triazine, 2-methylthio-4-terbutylamino-6-ethylamino-*s*-triazine, 2-methylsulfonyl-4-terbutylamino-6-amino-*s*-triazine and diaminohydroxy-*s*-triazine.

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