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Trifluralin photolysis in natural waters and under the presence of isolated organic matter and nitrate ions: kinetics and photoproduct analysis

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Abstract

The aquatic photochemistry of trifluralin has been investigated under simulated solar irradiation (Suntest apparatus) in different types of natural waters (sea, river and lake water) as well as in distilled water. In order to examine the effect of dissolved organic matter (DOM), photodegradation of the tested herbicide was also examined under the presence of humic and fulvic acids isolated from Pamvotis Lake at various concentrations. The influence of nitrate ions on the degradation kinetics was also examined. It was found that photodegradation proceeds via a pseudo first-order reaction in all cases and that the presence of DOM inhibits the photolysis reaction whereas rate constants measured in the presence of NO_3^- ions indicated higher degradation efficiency. Kinetic experiments were monitored by GC-FTD with half-lives ranging from 7.22 to 50.58 min. In addition Microtox bioassay (*vibrio fischeri*) was employed in evaluating the ecotoxicity of irradiated solutions. The major photodecomposition products formed mainly through dealkylation, cyclization and reduction processes were isolated by means of solid phase extraction (SPE) and were identified by GC-MS. Based upon this byproduct identification, a possible degradation pathway is proposed for the photolysis of trifluralin in aqueous media.

Keywords: Photodegradation; Trifluralin; Dissolved organic matter; Fate

1. Introduction

Contamination of surface waters and sediments from non-point sources is of major environmental concern. Pesticides contribute significantly to this problem due to their widespread usage on agricultural land from which they can be transported by surface runoff. A US survey [1] showed that pesticides were found in ∼40% of those watersheds identified as presenting the greatest risks to aquatic life or human health because of contaminated sediments. Detailed knowledge of the kinetics pathways of pesticides is pertinent in designing experiments to obtain reliable rate constants for use in assessing the fate and transport of pesticide pollutants in aquatic ecosystems. Trifluralin (2,6-dinitro-*N*,*N*-dipropyl-4-trifluoromethyl-benzenamine) a selective pre-emergency soil applied and soil incorporated herbicide representative of a growing list of *N*-substituted 2,6-dinitroanilines, is one of the most common herbicides (annual usage about 25 million lb) used to control grasses and weeds in a wide variety of agricultural crops since 1963 [2]. It has been characterized as moderately to highly toxic toward aquatic animals, including fish and invertebrates [2], and the US Environmental Protection Agency has classified it as a persistent bioaccumulative toxic substance (PBTs).

As a result of its widespread use, trifluralin has been frequently detected in environmental waters [3–5], air and precipitation, thus demonstrating the validity of the concerns outlined above.

It is therefore important to understand the fate of this herbicide in the environment in order to assess its environmental impact and potential health threats. Microbial degradation in soil has been reported with the active ingredients' half-live ranged from 1.5 to 6 months [6], while higher values (up to 12 months) can be correlated with dry or climatic conditions [7], something which could cause phytotoxicity problems for certain crops [8]. The environmental behavior of trifluralin especially in the soil system has been investigated in numerous field studies, the results of which have been reviewed [9]. Recently, the abiotic reduction of dinitroaniline herbicides including trifluralin [10] has been investigated.

Among the different transformation processes (biotic and abiotic), photodegradation is an important factor influencing

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the fate of organic micro pollutants in the field [11]. Several authors have reported on organic pollutants' photodecomposition under a variety of irradiation conditions and different solutions [12–17]. Most of these works use artificial solar sources of irradiation (xenon arc lamps) or ultraviolet (UV) light combined with catalyst particles such as TiO_2 or Fe_2O_3 [16,18–20].

Dissolved organic matter (DOM) present in natural waters plays an important role in regard to pesticide degradation. Being the primary light-absorbing species in surface water, DOM can either enhance [21,22] or inhibit the rate of photolysis [23,24].

Moreover, numerous studies over the last 20 years have provided unequivocal evidence that $OH^{\bullet}$ is generated in natural waters by the photolysis of nitrite and nitrate. In the early 1980s Korte and coworkers [25,26] pointed out that nitrate/nitrite photolysis could have a depolluting influence through the oxidation of organic compounds.

In addition the study of a contaminants' photochemical behavior is a key issue in terms of the formation of toxic transformation products. Therefore, toxicity assessment becomes necessary. Several methods and organisms for direct acute toxicity assessment are available [27]. Among them Microtox kit using the bacteria *vibrio fischeri* is especially rapid and reliable [28].

There is relatively little information in the literature regarding the fate of trifluralin in natural waters. This paper examines the phototransformation of trifluralin under laboratory conditions taking into consideration the major factors that may affect its environmental fate in natural waters such as DOM as well as the nitrate ions. The goals of this research are: (i) to determine the degradation kinetics of trifluralin in different environmental waters, (ii) to investigate the effect of humic and fulvic substances as well as the effect of the nitrate ions on the reaction rate, (iii) to assess the toxicity of the irradiated solution and (iv) to identify the transformation products formed by photolysis.

2. Experimental

2.1. Chemicals

Trifluralin (2,6-dinitro-*N*,*N*-dipropyl-4-trifluoromethylbenzenamine), was residue analysis grade, purchased from Riedel-de Häen (Seelze, Germany) and used without further purification. Humic and fulvic acids were isolated from Pamvotis Lake using the IHSS isolation method pre-established by Thurman and Malcolm in 1981 by the so-called XAD technique [29]. Pesticide grade *n*-hexane, methanol, dichloromethane and ethyl acetate were purchased from Pestiscan (Labscan Ltd., Dublin, Ireland). Sodium sulfate (pro-analysis) and $NaNO_3$ were obtained from Merck (Darmstadt, Germany) and Riedel de Haën, respectively. Styrenedivinylbenzene (SDB) copolymer extraction disks (47 mm) were purchased from 3 M Empore (St. Paul, USA), and a conventional filtration apparatus was from Supelco (Bellefonte, USA). Concentration of total organic carbon (TOC) in the water samples was measured with a Shimadzu Total Carbon 5000 Analyzer (TOC-5000 Shimadzu) using the High Temperature Catalytic Oxidation (HTCO) method.

Table 1
Characteristics of selected environmental waters

Water type	pH	Conductivity (μS/cm)	TDS[a]	TOC[b] (mg/l)	Salinity (‰)
Distilled	5.35	0.9	n.d.[c]	b.d.l.[d]	n.d.
Ionian Sea	7.62	50411	165	2.10	33.4
Louros River	7.81	382	208	2.93	0.40
Pamvotis Lake	7.87	516	361	11.03	0.44

[a] Total dissolved solids.
[b] Total organic carbon.
[c] Not determined.
[d] Below detection limit.

2.2. Water sampling

Natural waters used in the experiments were collected from the Epirus region of Greece (NW Greece) and were as follows: seawater (Ionian Sea), lake water (Pamvotis Lake) and river water (Louros River). The natural water samples were collected from the top meter of each water body in 2.5-l pre-cleaned amber glass bottles and stored at 4 °C prior to use. All water samples were used without previous treatment, filtration or sterilization. Their physicochemical characteristics are given in Table 1.

2.3. Chromatographic conditions

2.3.1. GC-FTD

The analysis of the photodegradation kinetics was performed by using a Shimadzu 14A gas chromatograph equipped with a DB-1 capillary column, 30 m × 0.32 mm i.d. (J&W Scientific, Folsom, CA). The temperature program was: 150 °C (2 min), 150–210 °C (5 °C/min), 210 °C (11 min), 210–270 °C (20 °C/min), 270 °C (0 min). Helium was used as both the carrier and the make-up gas with a flow rate of 1.5 and 40 ml/min, respectively. The detector gases were hydrogen (4 ml/min) and air (120 ml/min), and the ion source was an alkali metal salt (Rb_2SO_4) bonded to a 0.2 mm spiral of platinum wire. The temperatures were set at 240 °C for the injector and 280 °C for the detector.

2.3.2. GC-MS

A GC-MS, QP 5000 Shimadzu instrument equipped with a capillary DB-5-MS column, 30 × 0.25 mm × 0.25 μm, contained 5% phenylmethyl and 95% dimethylpolysiloxane (J&W Scientific, Folsom, CA) was used for the identification of the transformation products under the following chromatographic conditions: injector temperature 250 °C, oven temperature program 55 °C (2 min) to 210 °C (held 20 min)

at 5 °C/min and to 270 °C at 10 °C/min. Helium was used as the carrier gas at 1.0 ml/min. The interface was kept at 290 °C. The splitless mode was used for injection. The MS was operated in electron ionization mode with a potential of 70 eV and the spectra were obtained in full scan mode.

2.4. Photolysis in natural waters

Irradiation experiments were carried out in a 10 cm diameter cylindrical Duran glass UV-reactor by exposing 50 ml of the four different aqueous solutions (distilled, sea, river and lake water) of trifluralin (0.27 mg/l) under artificial solar irradiation. The irradiation was carried out using 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 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 an internal radiometer. The corresponding light dose for 1 h of irradiation was 2700 kJ/m^2. The temperature of samples did not exceed 25 °C using tap water cooling circuit for the UV reactor. A dark control experiment (in the absence of light) was also conducted in this series of experiments.

2.5. Photolysis in the presence of isolated humic/fulvic acids and nitrate ions

In order to examine the effect of DOM, aqueous solutions of trifluralin (0.27 mg/l) in distilled water (50 ml), were exposed to simulated solar irradiation using the Suntest apparatus and the same UV reactor in the presence of humic acid (HA) and fulvic acid (FA) isolated from Pamvotis Lake, concentrations of which were: 4, 8, 16 and 24 mg/l, respectively. The influence of NO_3^- ions on the reaction rate was also examined at concentrations close to the real environmental values (1.0, 2.5, 5.0 and 10.0 mg/l) at the same irradiation conditions.

2.6. Quantification and extraction procedure

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 water samples of 5 ml were withdrawn from 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 FTD, quantified by internal standard.

For the identification of the transformation products, 50 ml of the irradiation solutions were extracted separately at different time intervals, by means of solid phase extraction (SPE) as follows: SDB extraction disks were pre-conditioned with 10 ml of acetone for 2 h. In order to allow better extraction, 0.25 ml of methanol modifier was added to the residues. The disks were placed at the filtration apparatus and washed with 5 ml of solvent mixture dichloromethane:ethyl acetate (1:1, v/v) under vacuum, followed up with 5 ml of methanol for 3 min, with no vacuum applied. The disks were not allowed to dry and the samples were allowed to percolate through the disks under vacuum. The compounds that were entrapped to the disks were collected by using 2 × 5.0 ml of the elution mixture (dichloromethane:ethyl acetate, 1:1, v/v). The fractions were dried with sodium sulfate and finally evaporated to 0.1 ml under a gentle stream of nitrogen.

2.7. Calculation of half-life

Reaction kinetics was studied directly from the concentration versus time plots. The rate constants k were calculated from the first-order equation:

$$C_t = C_o\, e^{-kt} \quad (1)$$

where C_t is the herbicide concentration at time t, C_o is the initial concentration and k is the rate constant. When the concentration reduces to 50% of its initial value the half-life can be determined by the equation: $t_{1/2} = \ln 2/k$. Using a software program, the first-order rate constant (k) and the initial concentration of trifluralin were determined by least squares fitting of the data to a first-order kinetic equation.

2.8. Toxicity evaluation

The toxicity of trifluralin solution before and after irradiation (collected after different time intervals) was examined by a Microtox Model 500 Toxicity Analyzer. Freeze-dried bacteria, reconstitution solution, diluent (2% NaCl) and an adjustment solution (non-toxic 22% sodium chloride) were all obtained from Azur. The inhibition of the luminescence, compared with a toxic-free control to give the percentage of inhibition, was calculated following the established protocol and using the Microtox calculation program after contact times of 5 and 15 min.

3. Results and discussion

3.1. Photodegradation kinetics of trifluralin

Trifluralin was irradiated in different types of natural waters under simulated sunlight irradiation. The data were plotted as the concentration versus irradiation time. The pseudo first-order rate constants (k_{phot}) and the half-lives ($t_{1/2}$) for natural waters under simulated solar irradiation are summarized in Table 2.

Fig. 1 depicts the degradation curves of the herbicide in natural waters as well as in distilled water. Experimental data indicated that photolysis rate decreases in the following order: lake < river < sea < distilled water showing a strong dependence on the constitution of the irradiated media and

Table 2
Kinetic parameters of trifluralin photolysis in different aqueous media under simulated solar irradiation

Photolysis	$t_{1/2}$ (min)	k_{phot} (min^{-1})	R^2
Distilled water	11.81	0.0587	0.985
Sea water	23.89	0.0290	0.977
River water	29.49	0.0235	0.997
Lake water	50.58	0.0137	0.996
Humic[a] (4 mg/l)	16.08	0.0431	0.984
Humic (8 mg/l)	20.88	0.0320	0.991
Humic (16 mg/l)	24.06	0.0288	0.994
Humic (24 mg/l)	33.48	0.0207	0.962
Fulvic[a] (4 mg/l)	15.37	0.0451	0.985
Fulvic (8 mg/l)	18.83	0.0368	0.997
Fulvic (16 mg/l)	22.80	0.0304	0.995
Fulvic (24 mg/l)	31.08	0.0223	0.994
NO_3^-[a] (1 mg/l)	10.28	0.0674	0.989
NO_3^- (2.5 mg/l)	8.37	0.0828	0.996
NO_3^- (5 mg/l)	7.98	0.0869	0.988
NO_3^- (10 mg/l)	7.22	0.0960	0.983

[a] In distilled water.

especially on the concentration of DOM. The photodegradation rate was slower in natural waters than in distilled water: in other words as the DOM in natural waters increases the photolysis rate decreases. The retarded degradation rate could be attributed to the optical filter effect [30,31] since organic matter absorbed most of the photons emitted, thereby slowing down direct photochemical reaction. Moreover, particulate matter such as sediment particles and microorganisms suspended in a water column may scatter incident light, greatly reducing penetration of light beneath the surface. The very low solubility of the compound in water (0.27 mg/l) and its high K_{oc} value ($\log K_{oc}$ 5.07) indicates that this herbicide has also a tendency to associate with particulate matter and this fraction was never available to photolysis reactions. The retarded photodegradation rate in seawater is also consistent with $OH^\bullet$ scavenging by chloride ions [18].

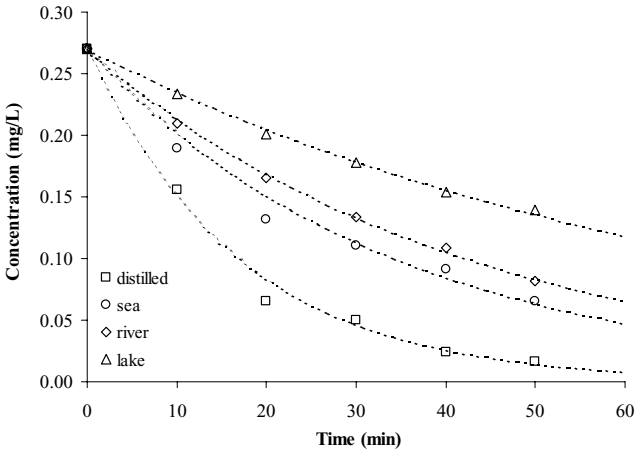

Fig. 1. Photodegradation of trifluralin in distilled, sea, river and lake water.

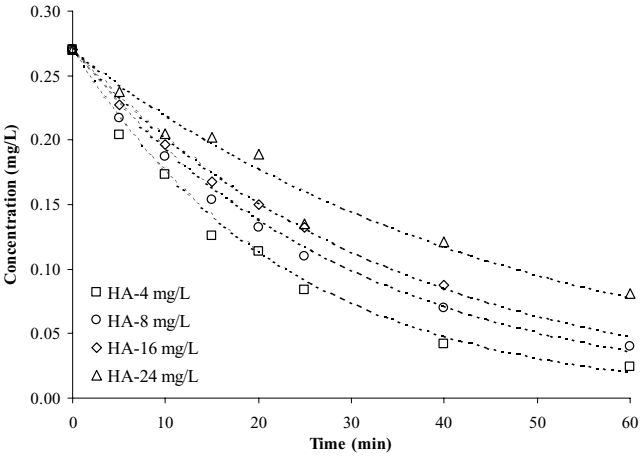

Fig. 2. Photodegradation of trifluralin in various concentrations of humic acids in distilled water under simulated solar irradiation.

Some studies have come up to the conclusion that DOM photolysis is considered a minor contribution to the concentration of $OH^\bullet$ that occurs in natural waters [26,32] but more recent observations suggest that DOM is a significant source of $OH^\bullet$ production, thus affecting the fate of the pollutants [9,33]. The results of this study suggest that DOM had a more important role in inhibiting the loss of the parent compound and this inhibition could be either the result of sorption of the contaminant [34,35], radical scavenging or light attenuation.

In order to verify the retardation effect observed in natural waters (attributed in DOM), experiments with the same initial concentration of trifluralin at various concentrations of isolated humic and fulvic substances were also conducted. In this case too, pseudo first-order dissipation curves were produced, allowing for the calculation of the rate constants (Figs. 2 and 3). In all cases the presence of DOM slowed down the rate of photolysis. For example, experiments conducted at concentrations: 4, 8, 16 and 24 mg/l of HA pro-

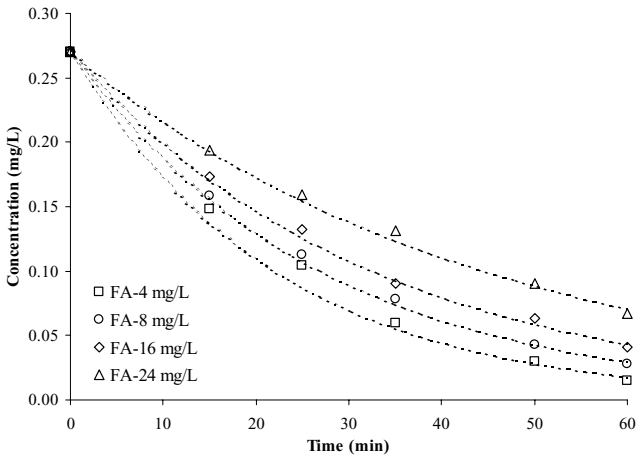

Fig. 3. Photodegradation of trifluralin in various concentrations of fulvic acids in distilled water under simulated solar irradiation.

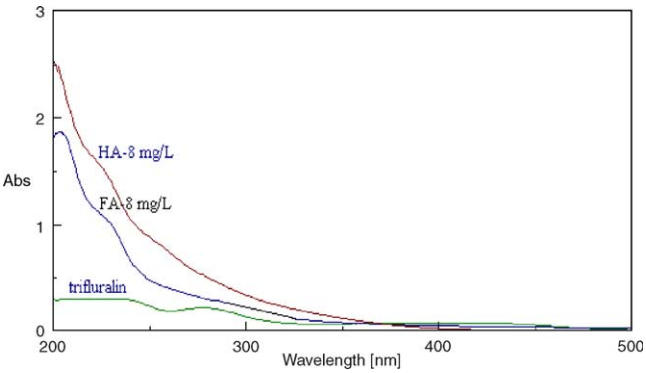

Fig. 4. UV spectra comparison of isolated humic and fulvic acids to trifluralin in distilled water.

duced rate constants of 0.0431, 0.0320, 0.0288 and 0.0207, respectively. The same tendency was also observed in the case of FA. The rate constants decreased as the concentration of FA increased: 0.0451, 0.0368, 0.0304, and 0.0223 at concentrations of 4, 8, 16, and 24 mg/l, respectively. Trifluralin absorbs some irradiation in the wavelength region emitted by the lamp source, and this wavelength range overlaps with the absorbance region of DOM (HA and FA), thus screening by DOM is significant (Fig. 4).

Besides competition of trifluralin and DOM for the available photons, the retarded photodegradation rates could also be attributed to binding of trifluralin to DOM. Adrian and Thorn have reported that aromatic amines such as trifluralin—a tertiary amine-entering the aquatic environment are subject to interesting reaction pathways like the covalent binding to DOM namely here HA and FA [36–38].

However, sensitized reactions by the presence of HA and FA can still play a role in limiting the persistence of trifluralin during photolysis, since a sixfold increase in DOM concentration (4–24 mg/l) resulted in a 23–65% decrease on the reaction rate. This could be explained by a combination of "inner filter" effect coupled with photosensitized reactions involving electronic energy transfer from triplet states of humic and fulvic acids to organic molecules as well as sunlight induced hydroxyl radical production.

Hamilton [19], Zafiriou [39], Zepp and coworkers [40,41] were the first to recognize nitrite/nitrate photolysis as a potential source of $^{\bullet}OH$ in natural waters which initiate rapid organic reactions. Of course, the exact mechanism of nitrate photolysis has been the subject of detailed investigation [42,43]. In the case we are studying here as illustrated in the kinetics diagram of trifluralin at four different NO_3^- concentrations in distilled water (Fig. 5) it seems that increasing nitrate concentrations decreased the half-life of trifluralin, thus the loss of the parent compound was predominantly the result of reaction with hydroxyl radicals. The degradation rate of trifluralin increases as much as 63% when 10 mg/l of NO_3^- is present in the water solution, in other words OH radicals produced from nitrate photolysis aided in its degradation.

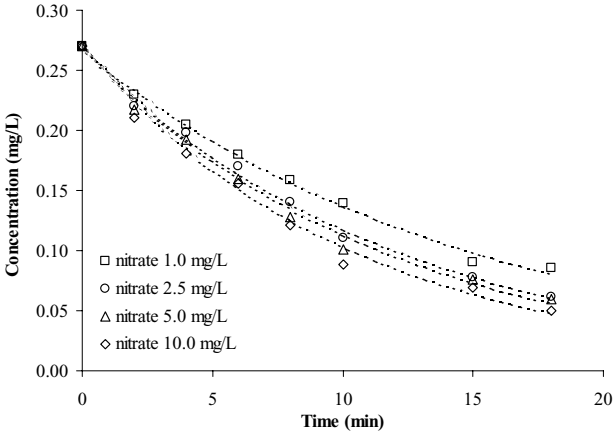

Fig. 5. Photodegradation of trifluralin at various concentrations of NO_3^- in distilled water under simulated solar irradiation.

3.2. Toxicity evaluation

The toxicity of the water samples was evaluated by monitoring changes in the natural emission of the luminescent bacteria *vibrio fischeri* (15-min incubation) when challenged with toxic compounds. The initial toxicity of trifluralin that showed an inhibition of 17% decreases rapidly in the first minutes of irradiation and an inhibition of less than 2% was observed after just 40 min of irradiation. After that time no measurable toxicity has been observed in the solution demonstrating that degradation of trifluralin yields to the formation of compounds non-toxic to the test organism. The inhibition of the luminescence bacteria *vibrio fischeri* during trifluralin photodegradation is shown in Fig. 6.

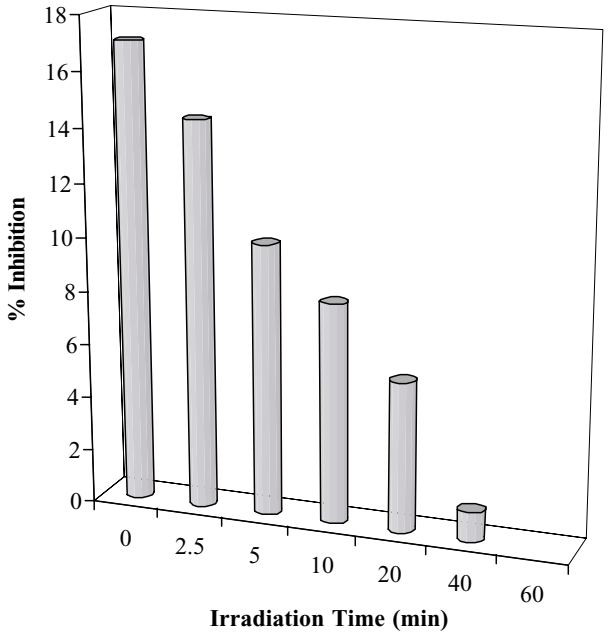

Fig. 6. Inhibition of the luminescence of bacteria *vibrio fischeri* as a function of the irradiation time.

Table 3
GC-MS-EI retention times and spectral characteristics of trifluralin and its transformation products

Compound		R_t (min)	m/z[a]
1	2,6-Dinitro-*N*-propyl-4-(trifluromethyl)benzenamine	25.40	293(5), 264(40), 248(15)
	Trifluralin	25.79	335(6), 306(100), 264(64)
2	3-Nitro-N^2-propyl-5-(trifluromethyl)-1,2-benzenediamine	26.56	263(64), 234(100), 216(91)
3	3-Nitro-5-(trifluromethyl)-1,2-benzenediamine	26.77	221(100), 203(54), 175(28)
4	2-Ethyl-4-nitro-6-(trifluromethyl)-1*H*-benzimidazole	27.18	258(100), 259(83), 212(81)
u1	Unidentified-1	27.52	296(7), 257(74), 185(100)
5	2-Ethyl-7-nitro-1-propyl-5-(trifluromethyl)-1*H*-benzimidazole	29.19	301(35), 244(48), 213(100)
6	2-Ethyl-1-propyl-5-(trifluromethyl)-1*H*-benzimidazole-7-amine	29.32	271(6), 242(6), 229(9)
7	2-Ethyl-6-(trifluromethyl)-1*H*-benzimidazole-4-amine	30.68	229(45), 228(39), 214(19)
u2	Unidentified-2	31.68	317(39), 260(89), 212(63)

[a] Relative abundance in parenthesis.

3.3. Degradation products

Up to seven compounds could be identified as possible degradation products during photodegradation process in natural waters. Their major GC-MS characteristics are summarized in Table 3. The total ion chromatogram obtained by GC-MS for the SPE extract of trifluralin solution after 5 and 15 min of simulated irradiation in lake water is shown in Fig. 7.

Photodecomposition of trifluralin generally involves three major routes: oxidative dealkylation of propylamines, cyclization and reduction of nitro groups.

The first product being produced seemed to be the mono-dealkylated derivative of the parent compound, compound (**1**), (R_t = 25.40 min). Compound (**1**) exhibited a molecular ion at $m/z = 293$ corresponding to the successive loss of the propyl group and fragments at $m/z = 264$ and 248, respectively. The photochemical *N*-dealkylation has been attributed to a free-radical oxidation [44] and has also been observed in the case of other pesticides like that of monuron [42] zectran and matacil [10]. Compound (**1**) associated to 2,6-dinitro-*N*-propyl-4-(trifluromethyl)benzenamine has also been detected by Klupinski and Chin [10], during the abiotic degradation of trifluralin.

Further photodegradation intermediates seemed to be formed by cyclization reactions. A modification of the free radical mechanism proposed by Doepp [45] to explain the photochemical formation of indole *N*-oxides from nitroaralkanes provides a plausible route from 2-nitroanilines to the benzimidazoles. By these means compounds (**5**) and (**4**) were apparently formed by a reaction between the propylamine α carbon and the NO_2 group of trifluralin and compound (**1**), respectively (Fig. 8), and were identified as 2-ethyl-7-nitro-1-propyl-5-(trifluoromethyl)-1*H*-benzimidazole (R_t = 29.19 min) and as 2-ethyl-4-nitro-6-(trifluoromethyl)-1*H*-benzimidazole (R_t = 27.18 min),

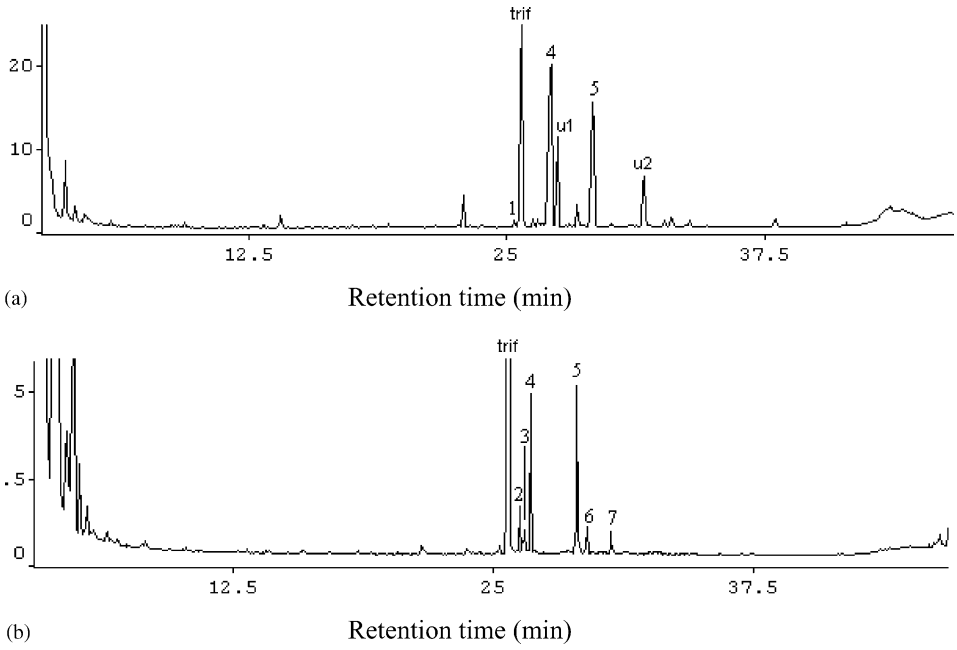

Fig. 7. Total ion chromatogram of trifluralin photodegradation in lake water, using SPE and GC-MS analysis at different irradiation time, (a) 5 min, and (b) 15 min.

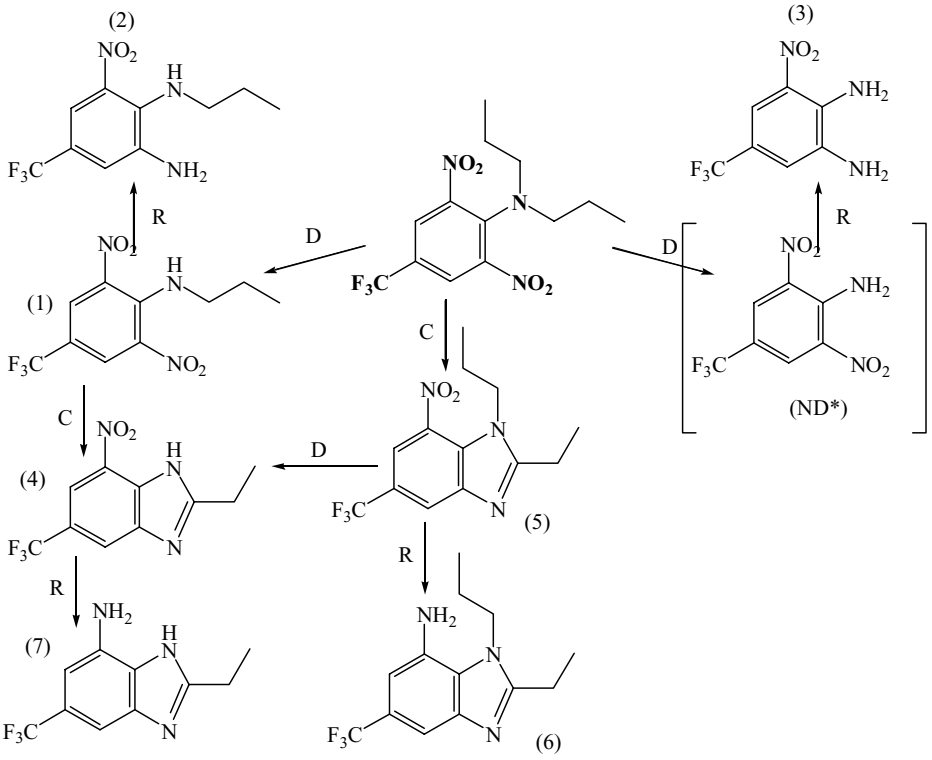

Fig. 8. Proposed photodegradation pathway of trifluralin in aqueous solutions. (*): not detected in this study.

respectively. The dealkylated benzimidazole (compound (**4**)) with a molecular ion at $m/z = 259$ and fragment ions at m/z: 258 and 212, most stable of the photoproducts, might persist in the environment long enough to be detectable as was the case with the corresponding compound from dinitramine [44]. It could also be formed by a dealkylation reaction from compound (**5**). The identification of compound (**5**) was made by using an identification program of NIST library with a fit value higher than 90%. It exhibited a molecular ion peak at $m/z = 301$ and fragment ions at $m/z = 244$ and 213, respectively.

Compounds (**5**) and (**4**) can be reduced by mechanisms not very clear in water media [46] through the formation of aryl hydroxylamines [10] to give compound (**6**) (R_t = 29.32 min) and compound (7) (R_t = 30.68 min), respectively, associated to 2-ethyl-1-propyl-5-(trifluromethyl)-1*H*-benzimidazole-7-amine and 2-ethyl-6-(trifluromethyl)-1*H*-benzimidazole-4-amine. These products have been also formed during the abiotic degradation of trifluaralin [10].

Compounds (**2**) and (**3**) are formed by a reduction of the NO_2 group to NH_2 from compounds (**1**) and 2,6-dinitro-4-(trifluromethyl)benzenamine, (compound ND), respectively. The latter, however, has not been identified in our study. Compound (**3**), (R_t = 26.77 min) the 3-nitro-5-(trifluoromethyl)-1,2-benzendiamine, exhibited a base peak at $m/z = 221$ and fragment ions at $m/z = 203$ and 175. These compounds too have been also identified during the abiotic degradation of trifluralin [10], showing that these routes account also for other process except photodegradation.

Two more unidentified peaks compounds (**u1**) and (**u2**) were considered as possible degradation intermediates since their amounts increased in the early steps of photolysis and then decreased with longer irradiation time.

Considering the opportunities for dealkylation, reduction and cyclization also available to the reaction intermediates of trifluralin photolysis, eventual photodecomposition of the herbicide to a largely irresolvable mixture of numerous trace products is reasonable. Therefore, a tentative and simple scheme (Fig. 8) can be drawn taking into consideration the main alteration processes for trifluralin photodegradation.

4. Conclusions

Photochemical behavior of trifluralin under simulated solar irradiation was under the scope of the present work. Degradation rates in natural waters were lower than in distilled water indicating thus a strong dependence on the composition of the water sample. DOM divided here into two fractions, namely humic and fulvic acids being isolated from aquatic humus (Pamvotis Lake), slows down the rate of photolysis. On the other hand, the presence of nitrate ions is accelerating the photolysis reaction. The formation of various transformation products proceeded via pseudo first-order reactions in all cases whereas their identity was determined by MS techniques. The bacterial toxicity of the aqueous tri-

fluralin solutions decreased with increasing irradiation time. Consequently, trifluralin photolysis produced compounds of lower toxicity or eventually non-toxic compared to the parent compound.

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References

[1] The Incidence and Severity of Sediment Contamination in Surface Waters of the United States, vol. 1: National Sediment Quality Survey, EPA 823-R-97-006, US Environmental Protection Agency, Office of Science and Technology, Washington, DC, 1997 (Chapter 4).
[2] Reregistration Eligibility Decision: Trifluralin, EPA-738-R-95-040, US Environmental Protection Agency, Office of Pesticide Programs, Washington, DC, 1996.
[3] P.D. Capel, T.A. Winterstein, S.J. Larson, Selected Data From Field Studies of Pesticide Runoff to Surface Waters, Water–Resources Investigations Report 004284, U.S. Geological Survey, National Water-Quality Assessment Program, Sacramento, CA, 2001 (Table 2).
[4] D.A. Lambropoulou, V.A. Sakkas, D.G. Hela, T.A. Albanis, J. Chromatogr. A 963 (2003) 107.
[5] T.A. Albanis, D.G. Hela, T.M. Sakellarides, I.K. Konstantinou, J. Chromatogr. 823 (1998) 59.
[6] F. Malterre, G. Grebil, J.-G. Pierre, M. Schiavon, Chemosphere 34 (1997) 447.
[7] H. Braunnschweiler, Agric. Sci. Fin. 1 (1992) 37.
[8] A.V. Jolley, P.K. Johnstone, J.A. Bos, Proceeding of the Ninth Australian Weeds Conference, Adelaide-South, Australia, 5–10 aout 1990, pp. 299–308.
[9] R. Grover, J.D. Wolt, A.J. Cessna, H.B. Schiefer, Rev. Environ. Contam. Toxicol. 153 (1997) 1.
[10] T.P. Klupinski, Y.P. Chin, Environ. Sci. Technol. 37 (2003) 1311.
[11] M. Fielding, D. Barcelo, A. Helweg, S. Galassi, L. Torstensson, P. Van Zoonen, R. Wolter, A. Angeletti, Pesticides in Ground and Drinking Water, Water Pollution Research Report 27, Commission of the European Communities, Brussels, 1992, p. 16.
[12] L. Scrano, S.A. Bufo, M. D'Auria, C. Emmelin, J. Photochem. Photobiol. A: Chem. 129 (1999) 65.
[13] V. Sakkas, D. Lambropoulou, T. Albanis, J. Photochem. Photobiol. A: Chem. 147 (2002) 135.
[14] N.S. Corin, P.H. Backlund, M.A.M. Kulovaara, Environ. Sci. Technol. 34 (2002) 2231.
[15] J.P. Da Silva, L.F. Vieira Ferreira, A.M. Da Silva, J. Photochem. Photobiol. A: Chem. 154 (2003) 293.
[16] G.A. Penuela, D. Barcelo, J. Chromatogr. A 823 (1998) 81.
[17] G.G. Choudry, G.R. Barrie Webster, Residue Rev. 96 (1985) 79.
[18] M. Mansour, E.A. Feicht, Chemosphere 28 (1994) 323.
[19] M.A. Valenzuela, P. Bosch, J. Jiménez-Becerrill, O. Quiroz, A.I. Páez, J. Photochem. Photobiol. A: Chem. 148 (2002) 177.
[20] I.K. Konstantinou, T.M. Sakellarides, V.A. Sakkas, T.A. Albanis, Environ. Sci. Technol. 35 (2001) 398.
[21] S. Canonica, U. Jans, K. Stemmler, J. Hoigne, Environ. Sci. Technol. 29 (1995) 1822.
[22] R.G. Zepp, P.F. Schlotzhaue, R.M. Sink, Environ. Sci. Technol. 19 (1985) 74.
[23] A. Torrens, B.G. Anderson, S. Bilboulian, W.E. Johnson, C.J. Hapeman, Environ. Sci. Technol. 31 (1997) 1476.
[24] J. Bachman, H. Patterson, Environ. Sci. Technol. 33 (1999) 874.
[25] H. Russi, D. Kotzias, F. Korte, Chemosphere 11 (1982) 1041.
[26] D. Kotzias, H. Parlar, F. Korte, Naturwissenschaften 69 (1982) 444.
[27] M.J. Ruiz, L. Lopez Jaramillo, M.J. Redondo, G. Font, Bull. Environ. Contam. Toxicol. 59 (1997) 619.
[28] A.R. Fernanndez-Alba, D. Hernando, A. Aguera, J. Caceeres, S. Malato, Water Res. 36 (2002) 4255.
[29] E.M. Thurman, R.L. Malcolm, Environ. Sci. Technol. 15 (1981) 463.
[30] R.A. Larson, E.J. Weber, Reaction Mechanisms in Environmental Organic Chemistry, CRC Press, Boca Raton, FL, 1994.
[31] F.H. Frimmel, D.P. Hessler, in: G.R. Helz, R.G. Zepp, D.G. Crosby (Eds.), Aquatic and Surface Photochemistry, CRC Press, Boca Raton, FL, 1994, pp. 137–147.
[32] G.P. Nilles, M.J. Zabik, J. Agric. Food Chem. 22 (1974) 684.
[33] D.G. Crosby, C.S. Tang, J. Agric. Food Chem. 17 (1969) 1041.
[34] A.M. Abdel-Wahab, J.E. Casida, J. Agric. Food Chem. 15 (1967) 479.
[35] W.H. Sharkey, W.E. Mochel, J. Am. Chem. Soc. 81 (1959) 3000.
[36] P. Andrian, F. Andreaux, R. Viswanathan, D. Freitag, I. Scheunert, Toxicol. Environ. Chem. 20/21 (1989) 109.
[37] K.A. Thorn, P.J. Pettigrew, W.S. Goldenberg, E.J. Weber, Environ. Sci. Technol. 30 (1996) 2764.
[38] K.A. Thorn, W.S. Goldenberg, S.J. Younger, E.J. Weber, in: J.S. Gaffney, N.A. Marley, S.B. Clark (Eds.), Humic and Fulvic Acids: Isolation, Structure and Environmental Role, American Chemical Society, Washington, DC, 1996, pp. 299–326.
[39] O.C. Zafiriou, J. Geophys. Res. 79 (1974) 4491.
[40] R.G. Zepp, D.M. Cline, Environ. Sci. Technol. 11 (1977) 359.
[41] O.C. Zafiriou, J. Joussot-Dubien, R.G. Zepp, R.G. Zika, Environ. Sci. Technol. 18 (1984) 358A.
[42] E. Rotlevi, A. Treinin, J. Phys. Soc. 69 (1965) 2645.
[43] J. Mack, J.R. Bolton, J. Photochem. Photobiol. A: Chem. 128 (1999) 1.
[44] R.A. Smith, Abstracts, 164th National Meeting of the American Chemical Society, NY, 1972.
[45] D. Doepp, Chem. Ber. 104 (1971) 1043.
[46] D.G. Crosby, Adv. Chem. Ser. No. 111 (1972) 173.