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# PHOTODEGRADATION OF TRIFLURALIN IN NATURAL WATERS AND SOILS: DEGRADATION KINETICS AND INFLUENCE OF ORGANIC MATTER

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The photochemical degradation of the herbicide trifluralin, a dinitroaniline, has been investigated in different types of natural waters (ground, marine, river, lake) and in distilled water as well as in soils characterized by different textures and compositions. Degradation kinetics was monitored under natural sunlight while the effect of humic acids (HA) on the degradation rate in natural waters was studied under laboratory conditions (Suntest apparatus). The photodegradation rate of the studied herbicide in different natural waters follows first-order kinetics with half-lives ranging from 12 to 29 h. The presence of dissolved organic matter (DOM) in the selected natural waters retarded the photoprocess relative to distilled water. Laboratory experiment has shown that the presence of HA inhibits the photolytic degradation of the herbicide. On the contrary, it was found that the degradation kinetics of trifluralin in soil is accelerated as the percentage content of organic matter increases. Photodegradation of trifluralin on the adsorbed phase (soils) gave depletion curves that can be well described by a first-order equation with half-lives varying from 15 to 38 h depending on the composition of the adsorbing media.

*Keywords:* Photodegradation; Trifluralin; Environmental fate; Organic matter

## INTRODUCTION

Since methyl aniline herbicides such as trifluralin, pendimethalin, profluralin, fluchloralin, etc. are widely used for weed control in crops, their behavior in the environment is vitally important. Trifluralin is a pre-emergence, soil-incorporated herbicide applied on many crops such as cotton, soybean, sunflower, and cereals as well as on oilseed rape. It has been in agricultural use since the early 1960s and is moderately persistent in soil. As a consequence of its widespread use, residue levels ranging from 0.016 to 30 µg/L have been detected in surface waters [1, 2]. Trifluralin has a low solubility, less than

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1 mg/L, and is tightly bound to the soil ( $K_{oc}$ : 4000–13 000) [3]. The active ingredient's half-life is between 1.5 and 6 months [4].

The persistence of trifluralin in cultivated soils following incorporation is highly variable, depending on several factors such as the depth of incorporation, the soil moisture and temperature, and the soil air and organic matter content. Moreover, it was found that, according to a microlysimeter study of trifluralin behavior in soil, its persistence in dry/cold climatic conditions could cause phytotoxicity problems [4].

Residues of trifluralin in soil surface layers are subject to loss via transport in runoff water or volatilization into the air. Seasonal losses in surface runoff are consistently less than 0.5% of the amounts applied, with concentrations in edge-of-field run-off water typically below 1.0  $\mu\text{g/L}$  [3]. Trifluralin is also dissipated by other dissipation processes, such as microbial and chemical, which are operative in soils, water, and sediments [3].

Among these different transformation processes (biotic and abiotic) it is well known that photodegradation is one of the most important factors influencing the fate of the pesticides in the environment [5]. Several authors have reported on pesticides photodecomposition under a variety of irradiation conditions and in different solutions [6–11].

Modeling pesticide behavior under laboratory conditions is a very useful tool for environmental studies but there is also a great need to conduct photodegradation studies in natural conditions, taking into consideration factors like the variation of temperature and the daily and seasonal variation of natural sunlight intensity [12].

The present work tries to approximate appropriate environmental conditions using natural solar irradiation on natural water and soil samples. In such media, dissolved and particulate organic matter as well as mineral materials could play an important role in the photochemistry of organic molecules. In these conditions photodegradation can occur by either direct or indirect absorption of light [13].

The aim of the present study is to determine: (i) the degradation kinetics of trifluralin in different natural waters and soils under environmental conditions and (ii) the effect of organic matter on the reaction rate.

## EXPERIMENTAL

### Chemicals

Trifluralin was residue analysis grade, purchased from Riedel-de Haen (Seelze, Germany) and used without further purification. Pesticide grade *n*-hexane, methanol, and acetone were purchased from Pestiscan (Labscan Ltd, Dublin, Ireland). Reagent grade sodium sulphate was supplied from Baker (Deventer, Holland). Ultra-pure water was obtained with a Milli-Q system from Millipore Co.

### Water Sampling

Natural waters used in the kinetics experiments were collected from the region of Epirus in Greece and included: ground and lake water (Pamvotis lake) both obtained from the territorial area of Ioannina, river water (Louros river) and sea water (Ionian sea) from the region of Preveza. The natural water samples were obtained from the top meter of each water body and refrigerated at 4°C prior to use. Their physicochemical characteristics are given in Table I.

TABLE I Characteristics of selected environmental waters

<i>Water type</i>	<i>pH</i>	<i>Conductivity</i> ( $\mu\text{S}/\text{cm}$ )	<i>TDS</i> ( $\text{mg}/\text{L}$ )	<i>TOC</i> ( $\text{mg}/\text{L}$ )	<i>Salinity</i> (‰)
Distilled	5.35	2.4	bdl	bdl	0.0
Ground	7.32	122	37	1.47	0.0
Sea	7.55	40 400	165	3.11	25.3
River	7.80	755	112	2.51	0.1
Lake	7.85	302	214	11.03	0.2

TDS = total dissolved solids; TOC = total organic carbon; bdl = below detection limit.

TABLE II Characteristics of selected soils

<i>Sampling site</i>	<i>Soil texture</i>	<i>pH</i>	<i>Sand</i> (%)	<i>Silt</i> (%)	<i>Clay</i> (%)	<i>OM</i> (%)	<i>CaCO<sub>3</sub></i> ( $\text{mg}/\text{L}$ )	<i>Conductivity</i> ( $\text{mS}/\text{cm}$ )
Preveza	SCL	7.0	43.7	24.0	33.3	0.90	0.63	0.65
Orestiada	CL	7.5	22.7	46.0	35.3	1.94	4.92	0.30
Lapsista	SL	6.5	55.1	36.0	8.9	5.76	2.64	2.68

OM = organic matter content; SCL = sandy clay loam; CL = clay loam; SL = sandy loam.

### Soil Sample Preparation

Three characteristic Greek soils were used for the kinetic experiments, being collected from the regions of Preveza, Orestiada, and Lapsista (Ioannina). Field-moist soils were passed through a 2 mm sieve to remove stones and large plant fragments and were then homogenized. Textural classes of soil samples were characterized as sandy clay loam (SCL), clay loam (CL) and sandy loam (SL) for the Preveza, Orestiada, and Lapsista regions, respectively. Their physicochemical characteristics are shown in Table II.

### Solar Irradiation of Natural Waters

Natural water samples, with no previous treatment of filtration or sterilization, were spiked with the pesticide by adding a methanol solution of the standard substance in order to give a nominal concentration of 0.25 mg/L. The aqueous samples thus obtained were put into capped quartz glass reservoirs of 1000 mL placed on the terrace of the Department of Chemistry and kept there during June 2001. A dark control experiment was also performed by exposing to the same environmental conditions dark quartz glass reservoirs filled with the same pesticide solutions and covered with aluminum foil.

Incident solar radiation was measured with a radiometer (Eppley Lab. Inc., Newport, Rhode Island, USA) in the wavelength range 285–2800 nm. The mean sunlight intensity at the beginning, middle, and end of the day, was estimated respectively as 265, 678 and 386  $\text{W}/\text{m}^2$  during June. The average total daily short-wave radiation for this period was 578  $\text{W}/\text{m}^2$ , with 10 h mean sunshine duration from sunrise to sunset. The mean daily air temperature was 24°C, maximum and minimum air temperatures were 33 and 12°C respectively.

### **Simulated Solar Irradiation in the Presence of Humic Acids**

Aqueous solutions of trifluralin (0.21 mg/L) in distilled water (50 mL), were exposed to simulated solar irradiation in a 10 cm diameter cylindrical Duran glass UV reactor in the presence of humic acids, the concentrations of which were: 4, 8, 16 and 24 mg/L, 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 light source was on the top of the reactor and an average irradiation intensity of 750 W/m<sup>2</sup> was maintained throughout the experiments measured by an internal radiometer. The temperature of samples did not exceed 25°C using tap water-cooling circuit for the UV reactor. A dark control experiment was also conducted.

### **Solar Irradiation of the Soil Sorbed Phases**

A thin layer of each soil (1 mm thickness) was obtained on chromatography (TLC) plates (20 × 20 cm each). Soils were homogenized and equilibrated with half of their weight of water sample, previously spiked with methanol standard solution in order to achieve an initial concentration in the range of 9–12 µg/kg, which is close to the usual field dosage. The content of methanol in the aqueous solution was kept below 10%. Then the plates were dried and exposed to natural sunlight during the summer period (June 2001). A dark control experiment was also carried out by covering analogous TLC plates of the same soil with aluminum foil.

### **Water Sample Extraction and Analysis**

Water samples of 5 mL were withdrawn from the glass reservoirs and the UV-reactor at different time intervals. The samples were extracted twice with 2.5 mL *n*-hexane for one minute using a vortex, dried with a small amount of Na<sub>2</sub>SO<sub>4</sub> and finally analyzed by gas chromatography coupled with a flame thermoionic detector (FTD).

### **Soil Sample Extraction and Analysis**

A 2 × 2 cm zone of each TLC plate was scraped off and extracted twice with 10 mL acetone using a vortex. The acetone soil suspension was sonicated and centrifuged at 4000 rpm for 10 min to separate the supernatant from the soil residue. The volume of the combined supernatants was fixed at 5 mL and this was later analyzed by the GC-FTD system.

### **Chromatographic Conditions**

The analysis was performed 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. The detector gases were hydrogen and air, and the ion source of the FTD was an alkali metal salt (Rb<sub>2</sub>SO<sub>4</sub>) bonded to a 0.2 mm spiral of platinum wire. The temperatures were set at 240°C for the injector and 250°C for the detector.

## RESULTS AND DISCUSSION

### Photodegradation in Water

Photodegradation rates of trifluralin in different natural waters follow a first-order degradation curve

$$C_t = C_0 e^{-kt}, \quad (1)$$

where  $C_t$  is the herbicide concentration at the time  $t$ ,  $C_0$  is the initial concentration, and  $k$  is the rate constant. The half-life time ( $t = t_{1/2}$ ) corresponds to a period of time at which the pesticide concentration equals half of its initial concentration and is given by the equation

$$t_{1/2} = \ln \frac{2}{k}. \quad (2)$$

The photodegradation constants ( $k$ ) were calculated by subtracting the kinetic constants of the apparent degradation reactions and those of the degradation due to hydrolysis, volatilization, adsorption (blank experiments). In this way the considered  $k$  constants and  $t_{1/2}$  refer to the real photochemical reaction excluding the contribution of other factors (Table III).

Figure 1 shows the degradation curves of the pesticide in natural waters as well as in distilled water. The photolysis rate decreases in the following order: lake < river < sea < ground < distilled water.

The photodegradation rate was slower in natural waters than in distilled water; in other words: as the DOM in natural water increases, the photodegradation rate decreases. The above result could be attributed to the optical filter effect (quenching) of the organic matter, which could act as one of the most important sunlight absorbing components of the aquatic environment [13,14]. 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. In other cases, sorption protects substrates from photolysis, possibly by competitive light attenuation, by migration of the pollutant into regions of the particle where light does not penetrate, or by quenching of the excited states of substrates by constituents of sorbent particles [13].

However, a sensitization effect of humic and other substances of natural waters cannot be excluded. The resulting excited states of the DOM, and reactive transients produced from DOM, could participate in energy transfer, electron transfer, and free radical reactions that affect the fate of aquatic pollutants [13]. The effect of humic substances on the photolysis rate of trifluralin was studied in laboratory conditions (Suntest apparatus) at different concentrations of HA (4–24 mg/L) in distilled water (Fig. 2).

TABLE III Half-lives and photolysis rates in natural waters

<i>Water type</i>	$k_{phot} \times 10^{-2}$ (h <sup>-1</sup> )	$t_{1/2}$ (h)
Distilled	5.73	12.1
Ground	4.47	15.5
Sea	3.16	22.2
River	3.00	23.1
Lake	2.36	29.4

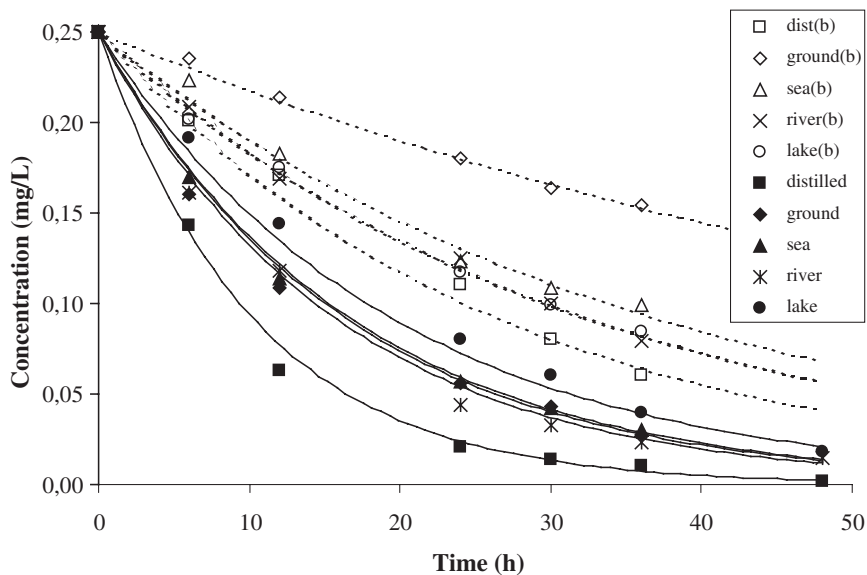


FIGURE 1 Photodegradation of trifluralin in natural waters under solar irradiation. (b) = blank experiment.

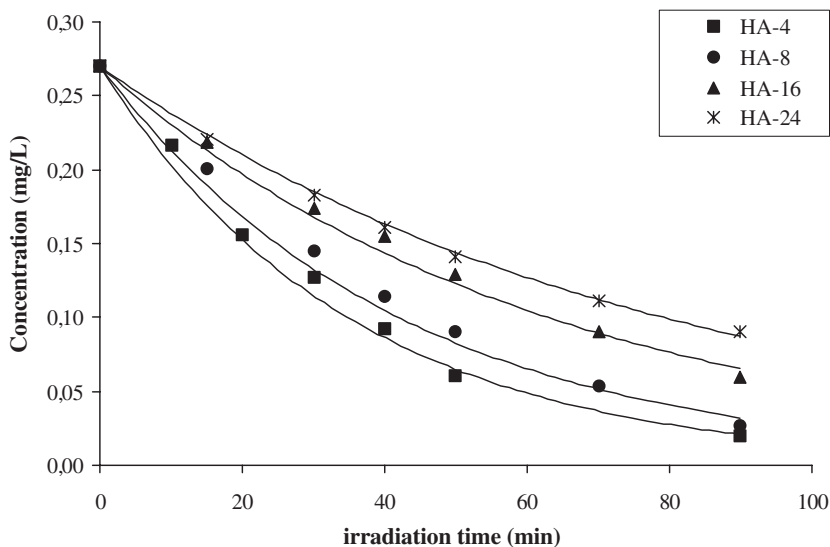


FIGURE 2 The effect of humic acids on the photodegradation rate of trifluralin in distilled water.

It is obvious that as the concentration of humic acids in solution increases the photodegradation rate decreases. The half-lives as well as the photolysis rates of the herbicide in the presence of humic acids are presented in Table IV. This observation confirms the quenching effect (optical filter effect), that was observed in natural waters under solar irradiation. However, a sensitization effect by other constituents present in natural waters cannot be excluded. Nitrite and nitrate ions absorb light and undergo homolysis to produce free radicals [15]. It is probable that in nitrite and nitrate photolysis, the dominant process is the production of hydroxyl radical which accelerates

organic reactions. Other ions such as calcium and magnesium, also accelerate the photodegradation because they take part in complexation reactions enhancing the photolysis of organic compounds [10].

The data in this study are in contrast with other studies [7], which indicate a sensitization effect of humic substances, indicating that DOM competes for UV-Visible light decreasing the photodegradation rate. In other words the sensitization effect is hidden by the strong filtering effect.

### Photodegradation in Soil

All measured reaction rates (in darkness and under irradiation conditions) of adsorbed herbicide followed a first-order degradation curve and their half-lives were calculated from Eq. (2). In this case, too, the kinetics constants were calculated by subtracting the kinetic constants  $k_{app}$  of the apparent degradation reactions and those due to hydrolysis, volatilization, and adsorption (blank experiment).

First-order degradation curves were observed in the three selected soils studied during the observation time. In all cases, trifluralin was more rapidly degraded after 24 h of irradiation than in the dark controls (Figs. 3–5).

The half-lives of trifluralin photodegradation (Table V) ranged between 15 and 38 h depending on the composition of sorbing media.

TABLE IV Kinetic parameters of trifluralin degradation in distilled water in the presence of HA under simulated solar irradiation

HA concentration (mg/L)	$k_{phot} \times 10^{-2}$ (min <sup>-1</sup> )	$t_{1/2}$ (min)	$R^2$
(HA-4)	2.85	24	0.994
(HA-8)	2.37	29	0.985
(HA-16)	1.58	44	0.989
(HA-24)	1.26	55	0.997

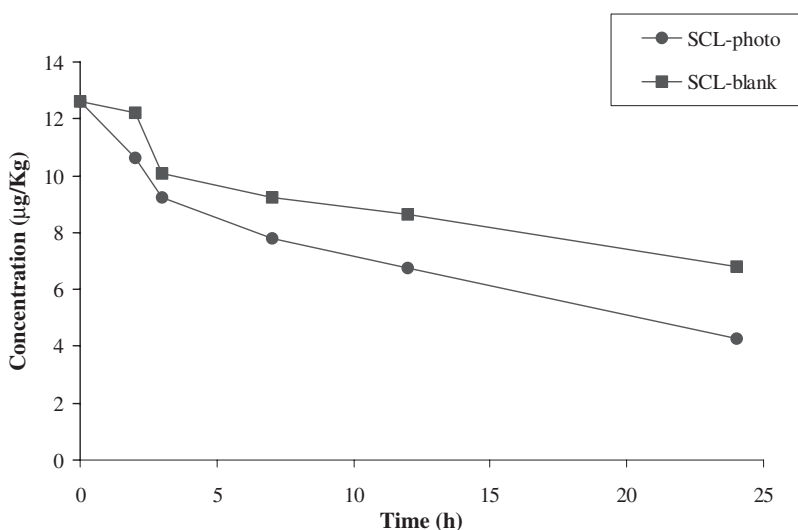


FIGURE 3 Photolysis of trifluralin in SCL soil under solar irradiation.



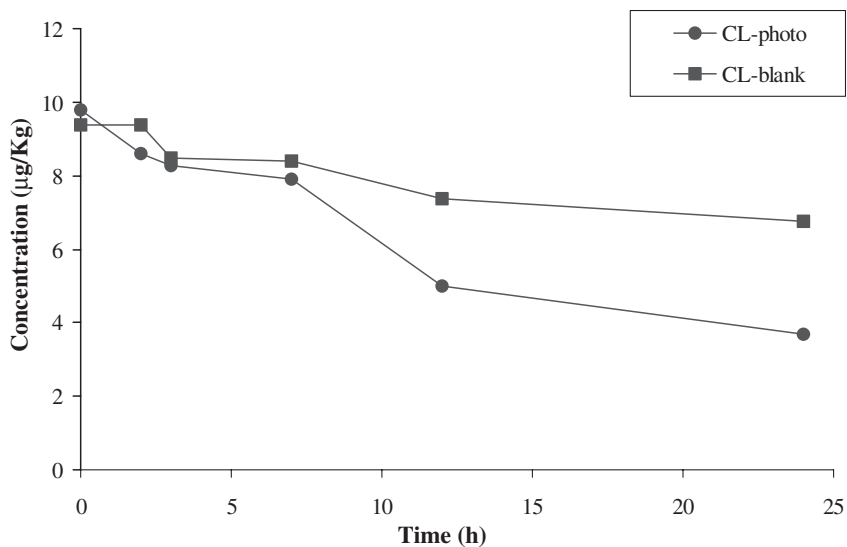


FIGURE 4 Photolysis of trifluralin in CL soil under solar irradiation.

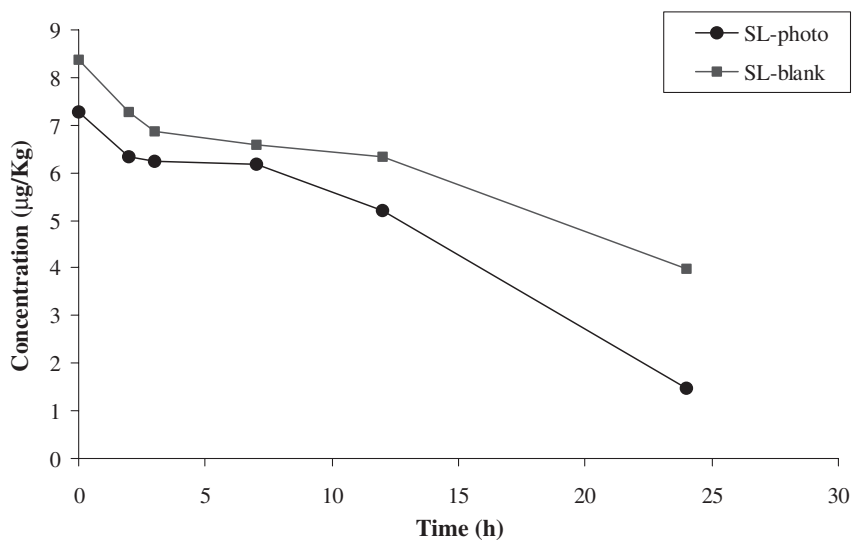


FIGURE 5 Photolysis of trifluralin in SL soil under solar irradiation.

TABLE V Half-lives and photolysis constants of trifluralin in soil

Soil type	$t_{1/2}$ (h)	$k_{phot} \times 10^{-2}$ ( $\text{h}^{-1}$ )
SCL	38.0	1.82
CL	24.2	2.86
SL	15.3	4.54

The results demonstrate that the photolysis rate of trifluralin increases with an increase of the organic matter content in soil. Schematically, the reactivity in soil follows the order: SL > CL > SCL.

On dry, sunlight-exposed surfaces, photolysis may dominate other transformation pathways that are, on the contrary, favored under conditions found in bulk soil. Direct photolysis rates of soil-sorbed pesticide are substantially slower than for pesticide dissolved in distilled water, presumably because of light attenuation in the soil [16]. In soil, photolysis occurs within a shallow surface zone, the depth of which depends on soil characteristics and the mechanism of photodegradation. Light absorption and photolysis of organic contaminants will be influenced by sorption reactions, which are related to the soil organic matter content, and singlet oxygen formation. Both direct and indirect process could be occurring depending on the depth. Hebert and Miller [16] conclude that the vertical depth of direct photolysis on the soil surface will be restricted to a region of approximately 0.2–0.3 mm. Mean indirect photolysis depths were reported to be greater than 0.7 mm for outdoor experiments. However, several studies [17–22] have indicated that humic acids are capable of acting as sensitizers for the production of reactive intermediates such as singlet oxygen ( $^1\text{O}_2$ ), hydroxyl radicals ( $\cdot\text{OH}$ ), super oxide anion ( $\text{O}_2^-$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and peroxy radicals ( $\text{ROO}\cdot$ ). The results of the present study confirmed that in soil the sensitizing effect of organic matter is greater than the scattering effect as the photodegradation rates were increased in soils rich in organic substances.

Natural organic matter is an exceedingly complex material that significantly affects the fate and transport of pollutants in the environment. However, further research is needed to evaluate the role of organic matter in such photolytic reactions.

## CONCLUSIONS

The photochemical behavior of the dinitroaniline herbicide trifluralin in natural waters and soils under environmental conditions has been investigated. In addition, the effect of dissolved organic matter, such as humic substances, on kinetics has been studied under laboratory conditions. In all cases, first-order reaction kinetics was observed. The results demonstrated that the degradation rate in natural waters was lower than in distilled water showing a strong dependence on the composition of water samples and especially on the dissolved organic matter, which provides an optical filter effect. On the contrary, the degradation rate of trifluralin in the soil-sorbed phase was higher as the organic matter was increasing. This could be attributed to the different origin and type of organic matter present in the soil matrix, which could influence the photoprocess differently by sensitizing the degradation of the herbicide.

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