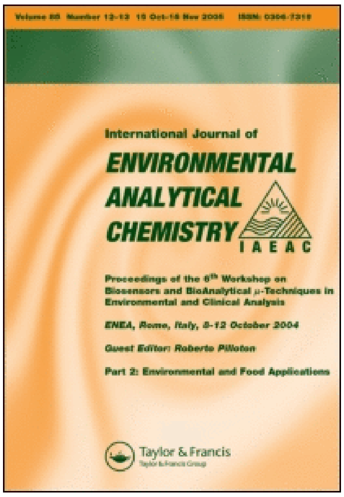

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Surface Adsorption and Photo-Reactivity of Sulfonylurea Herbicides

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To cite this Article Albanis, Triantafyllos A. , Bochicchio, Dominga , Bufo, Sabino A. , Cospito, Isabella , D'Auria, Maurizio , Lekka, Marilena and Scrano, Laura(2002) 'Surface Adsorption and Photo-Reactivity of Sulfonylurea Herbicides', International Journal of Environmental Analytical Chemistry, 82: 8, 561 — 569

To link to this Article: DOI: 10.1080/03067310290007822

URL: http://dx.doi.org/10.1080/03067310290007822

Intern. J. Environ. Anal. Chem., Vol. 82, No. 8–9, pp. 561–569

SURFACE ADSORPTION AND PHOTO-REACTIVITY OF SULFONYLUREA HERBICIDES

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(Received 24 August 2001; In final form 31 December 2001)

Photodegradation of two sulfonylurea herbicides, triasulfuron and thifensulfuron-methyl adsorbed on Preveza or Nea Malgara soils (Greece) was studied in outdoor and laboratory experiments. Herbicides on adsorbed phase and kept in the dark were characterised by a high reactivity, giving depletion curves that can be all described by a first order equation. In the irradiation experiments the kinetic behaviour of photodegradation was complex and characterised by a double step photoreaction. After a first period varying from 8 to 24 h the rate of reaction was reduced to 7–31% of the initial rate. The kinetic constant related to the degradation of triasulfuron practically showed the same values of those obtained for thifensulfuron-methyl. The half-lives obtained on Nea Malgara soil were generally higher than those obtained using Preveza soil. The observed behaviour is explained considering the photochemical properties of the herbicides, and the organic matter content of the soils.

Keywords: Triasulfuron; Thifensulfuron-methyl; Adsorbed phase; Soil; Photodegradation; Kinetics

INTRODUCTION

In the last decade, a new class of herbicides named sulfonylureas has been developed and offered on the market. Some of the reasons for the rapid and good acceptance of sulfonylureas include their low application rate and favourable environmental and toxicological properties [1].

Triasulfuron (**1**) is a sulfonylurea herbicide with molecular formula $C_{14}H_{16}ClN_5O_5S$ (Fig. 1). It is a post-emergence herbicide utilised for the treatment of wheat, barley, rye, and oats. It is used in low doses ($37\,g\,ha^{-1}$, for a commercial formulation with 20% active ingredient) and shows very low toxicity ($LD_{50} > 5000\,mg\,kg^{-1}$ on rats).

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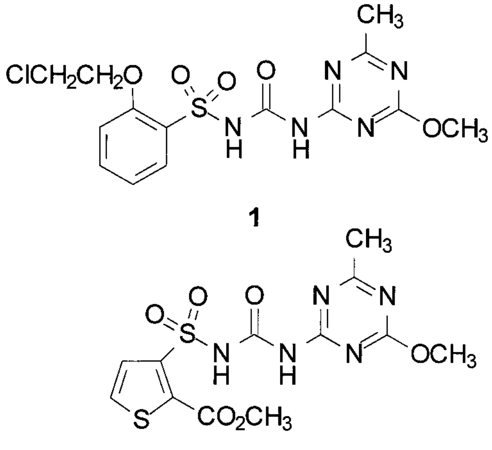
ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/03067310290007822



1

2

FIGURE 1 Triasulfuron (**1**) and thifensulfuron-methyl (**2**).

Thifensulfuron-methyl (**2**) is another member of the same family with molecular formula $C_{12}H_{13}N_5O_6S_2$ (Fig. 1). It is a post-emergence herbicide used to control dicotyledonous weeds in maize cultures. All these compounds act through the inhibition of acetolactate synthase, an enzyme involved in the cellular growth of plants [2–4].

Hydrolysis and microbiological action are the most important degradation pathways for this class of compounds. The absorption of light can be a further degradation way. Recently, the photochemical degradation of triasulfuron (**1**) in aqueous solution has been reported [5]. The irradiation at 254, 300 and 360 nm led to pseudo first order degradations of **1** producing some metabolites such as 2-chloroethoxybenzene and 2-methoxy-4-methyl-6-triazinylurea. Unfortunately, the use of an aqueous solution did not allow distinguishing between photochemical reaction and hydrolysis.

The degradation of triasulform (**1**) in field experiments has been evaluated at 5–10°C and humidity lower than 50%, giving a half-life of 200 days, while in alkaline soil hydrolysis can be considered a negligible process [2,5]. The degradation in the soil through hydrolytic and microbiological processes of thifensulfuron-methyl (**2**) has been extensively studied [6–14].

Data available on the fate of these herbicides in the environment do not include the photochemical behaviour on adsorbed phase (soil). In order to fill this lack of information on an important degradation pathway in the environment, we report here our results about the photochemical degradation of triasulfuron and thifensulfuron-methyl on two Greek soils.

EXPERIMENTAL

Chemicals

All solvents (pesticide grade), reagents (analytical grade) and filters (disposable sterilised packet) were purchased from Fluka and Sigma–Aldrich (Milan, Italy). Ultra

TABLE I Physical and chemical properties of selected soils

Soil	*Sand %*	*Silt %*	*Clay %*	*pH*	*Organic matter %*
Preveza	45	22	33	7.0	0.9
Nea Malgara	31	50	19	7.1	2.3

pure water was obtained with a Millipore Milli-Q system (Mississauga, ON, Canada). Triasulfuron (98%; MW 401.8; V.P. 100 fPa at 20°C; pK_a 4.5), 1-[2-(chloroethoxy)-phenylsulfonyl]-3-(4-methoxy-6-methyl-1,3,5-triazin-2yl) urea (CAS RN [*82097–50–5*], and thifensulfuron-methyl (98.8%; MW 387.4; V.P. 17 nPa at 25°C; pK_a 4.0 at 25°C), methyl 3-[3-(4-methoxy-6-methyl-1,3,5-triazin-2yl)ureidosulphonyl] thiophene-2-carboxylate (CAS RN [*79277–27–3*]) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

UV spectra of triasulfuron and thifensulfuron-methyl in anhydrous acetonitrile were recorded on a Cary 2300 spectrophotomer (Varian, Harbor City, CA).

Adsorbed Phase Preparation

Two soils from Greece were sampled: a *sandy clay loam* soil from Preveza region, in Southern Epirus, and a *silt loam* soil from Nea Malgara region. Physical and chemical properties of selected soils are shown in Table I. Soils were sieved (2 mm) and sterilised before their use in order to avoid microbiological degradation [14]. Soils were added with sodium azide (0.05%) and incubated for 24 h (FTC 90E Refrigerated Incubator, Velp Scientifica, Milan, Italy).

Standard solutions of the herbicides were prepared dissolving 0.0101 g of triasulfuron or 0.0122 g of thifensulfuron-methyl in 98% methanol (10 mL). The solutions were sonicated for 5 min, in order to reach complete dissolution of herbicides, and were stored in the dark at 4°C. Aqueous solution (80 mL) previously spiked with 1 mL of the triasulfuron or thifensulfuron-methyl standard solution was added drop by drop to 160 g of soil sample with gentle stirring. The soil paste thus obtained was spread on two glass TLC plates (20 × 20 cm) in order to obtain 1 mm thick soil layer. The plates were air dried in the darkness at room temperature for 1 day. The first plate was used for irradiation experiments, the second one as control in dark conditions.

Irradiation Experiments

Photochemical reactions were performed by using a solar simulator (Suntest CPS+, Heraeus Industrietechnik GmbH, Hanau, Germany), equipped with a xenon arc (1.1 kW) that was protected with a quartz plate (total passing wavelength: $300\,\text{nm} < \lambda < 800\,\text{nm}$). During xenon irradiation samples were maintained at 20°C. Natural solar light irradiation was also carried out in the case of triasulfuron on Preveza soil, protecting TLC plates with a quartz chamber. Incident solar radiation was detected with a radiometer (Eppley Lab., Newpot, RI) that measured radiation in the wavelength range 280–2800 nm. The average total daily short-wave radiation for the experiment period (October, 2000) was $438\,\text{W}\,\text{m}^{-3}$, with an 8 h mean sunshine duration from sunrise to sunset.

Analytical Procedure

Samples for the determination of reaction kinetics were obtained scraping off, at various illumination times, 1 by 1 cm width strips of the soil layer from the TLC plates. The material was put into a test-tube and weighed. Then, methanol (10 mL) was added. The mixture was stirred (Vortex) for 1 min and placed for 10 min in a sonication bath. The solution was separated and the procedure was repeated other two times by using 5 mL of methanol each. The resulting methanol solution (20 mL) was centrifuged (10 min; 4000 rpm) and concentrated by fluxing nitrogen; finally volume solution was adjusted to 5 mL. The samples were filtered and kept in the darkness at 4°C.

The analyses were carried out by using an SPD-M10A Shimadzu HPLC (Kyoto, Japan), equipped with a diode array detector. A Supelcosil LC-18-5 µ column (25 cm × 4.6 mm ID) was used. The mobile phase was water (pH = 2.75, acetic acid) and acetonitrile with the following gradient: $t = 0$ min, 95% water; $t = 10$ min, 80% water; $t = 20$ min, 60% water. A flux of 1 mL min^{-1} was used. The chromatograms were revealed by using $\lambda = 230$ nm for triasulfuron (T_f, 29.8 min) and $\lambda = 254$ nm in the case of thifensulfuron-methyl (T_f, 24.5 min). The calibration plots were performed in the concentration range 0.25–8 mg L^{-1} giving a linear response of both herbicides with $r^2 > 0.999$. Detection limits were found to be 0.04 and 0.13 mg L^{-1} for a triasulfuron and thifensulfuron-methyl, respectively.

RESULTS AND DISCUSSION

Photochemical Properties

The UV-spectrum of triasulfuron showed absorption maxima at $\lambda = 224$ ($\log \varepsilon = 4.48$) and $\lambda = 280$ nm ($\log \varepsilon = 4.39$). The UV-spectrum of thifensulfuron-methyl showed absorption maxima at $\lambda = 254$ ($\log \varepsilon = 4.31$), $\lambda = 288$ ($\log \varepsilon = 4.11$), $\lambda = 312$ ($\log \varepsilon = 3.82$) and $\lambda = 326$ nm ($\log \varepsilon = 3.73$). Recorded absorptions of herbicides are consistent with the filtered emissions of the xenon lamp (total passing wavelength: 300 nm < λ < 800 nm) and the UV-B region of sunlight irradiation (280–315 nm). Absorptions of thifensulfuron-methyl are better covered both by simulated and natural solar emissions.

Adsorbed Phase Reactions

Soils were spiked with 6.33 and 7.62 mg kg^{-1} of triasulfuron or thifensulfuron-methyl, respectively; but with first extractions ($t = 0$) a large part of spiked quantities was not found (C_0 values in Table II). Extraction of thifensulfuron-methyl was more effective than triasulfuron; only 32 and 58% of the last herbicide was extracted from Nea Malgara and Preveza soil, respectively; thifensulfuron-methyl was extracted as 62 and 71% of applied amount from the same soils. In both cases herbicides were more extractable from Preveza soil than Nea Malgara soil.

These effects can be due to soil retention and formation of "bond residues", which cannot be extracted with methanol. It is not fortuitous that the more organic soil from Nea Malgara region retained higher quantities of both herbicides. For this reason, we tried to extract more quantity of herbicides using (in order of extracting strength); acetonitrile, ethyl acetate, acetone, 1 : 2 (v : v) mixture of ethyl acetate/water,

TABLE II Kinetic parameters of herbicide reactions on adsorbed phase: n, reaction order; r^2, determination coefficient; C_0, extractable quantity at initial time; τ, half-life; k, kinetic constant

Soil	*Herbicide*	*Irradiation/* h	*n*	r^2	C_0 mg/kg	τ h	*k* h^{-1}
Preveza	Triasulfuron	Suntest 0–8	1	0.975	3.68	6.07	0.1142
		Suntest 8–48	1	0.980	1.89	21.5	0.0322
		Dark 0–48	1	0.992	3.68	70.7	0.0098
Preveza	Triasulfuron	Solar 0–24	1	0.998	3.68	6.69	0.1036
		Solar 24–48	1	0.982	0.57	24.1	0.0288
		Dark 0–48	1	0.995	3.68	26.0	0.0267
Preveza	Thifensulfuron-methyl	Suntest 0–20	1	0.983	5.44	6.91	0.1003
		Suntest 20–48	1	0.977	1.10	21.9	0.0317
		Dark 0–48	1	0.998	5.44	24.2	0.0286
Nea Malgara	Triasulfuron	Suntest 0–10	1	0.995	2.02	15.3	0.0452
		Suntest 10–48	1	0.991	1.29	82.5	0.0084
		Dark 0–48	1	0.991	2.02	198	0.0035
Nea Malgara	Thifensulfuron-methyl	Suntest 0–12	1	0.991	4.76	7.27	0.0954
		Suntest 12–48	1	0.991	1.71	91.2	0.0076
		Dark 0–48	1	0.998	4.76	33.5	0.0207

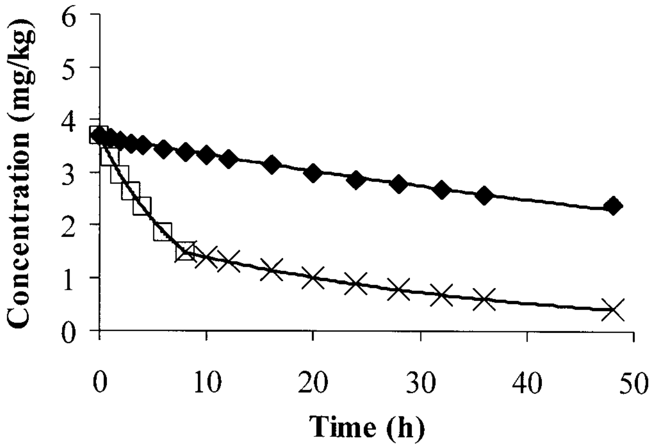


FIGURE 2 Concentration of triasulfuron on Preveza soil: photodegradation under xenon arc irradiation (Suntest), first rate (☐), second rate (×): reaction in the dark (◆).

1 : 1 (v : v) mixture of acetone/water; but we were not able to obtain a significant increasing of the herbicide recoveries, improvements of which ranged from 1.8 to 9.2%. On the other hand, observing the behaviour of herbicides kept in the dark, we note that they are characterised by a lasting reactivity, giving depletion curves that can be described by a first order equation (Table II, Figs. 2–6). The loss of herbicide molecules continued all through the 48 h experiment time. On the basis of these results, we suppose that a variable fraction of both herbicides could be lost by volatilisation and/or hydrolysis during the preparation of treated soil samples (considering also the time for the soil layer drying on glass plates) and the first experiment hours; afterwards, adsorption worked protecting the xenobiotic molecules from other reactions because of the molecular rearrangement of herbicides into the adsorption sites of soils. In any case,

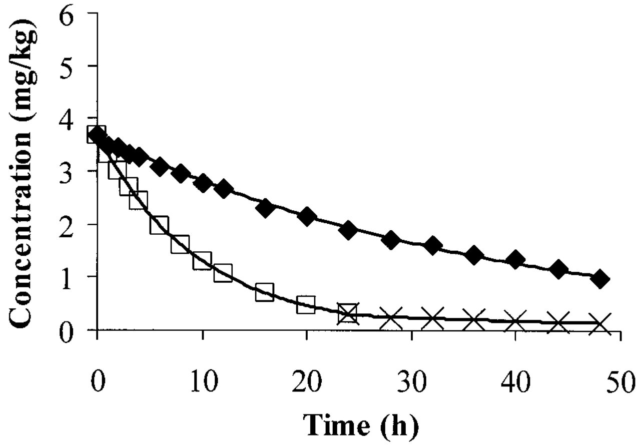


FIGURE 3 Concentration of triasulfuron on Preveza soil: photodegradation under natural solar irradiation, first rate (□), second rate (×); reaction in the dark (◆).

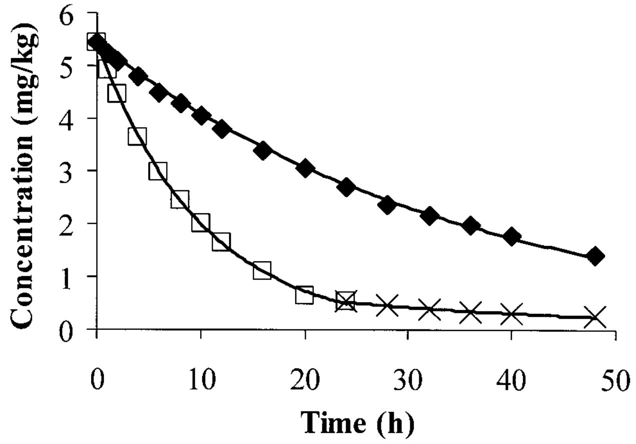


FIGURE 4 Concentration of thifensulfuron-methyl on Preveza soil: photodegradation under xenon arc irradiation (Suntest), first rate (□), second rate (×); reaction in the dark (◆).

retention on adsorbed phase has to be considered as one of the major factor of "no-extractability" for studied herbicides.

We decided to continue with using methanol, which gave cleanest chromatograms with respect to other extracting solvents and solutions. In fact, more organic substances, naturally occurring in the soil, were dissolved in the tested solvents and mixtures particularly from Nea Malgara soil.

Photochemical Degradation *vs.* Absorption

Kinetic parameters of herbicide reactions on both soils are referred in Table II.

All measured reaction rates (in darkness and under irradiation conditions) of adsorbed herbicides followed a first order degradation curve, $C_t = C_0 \exp(-kt)$,

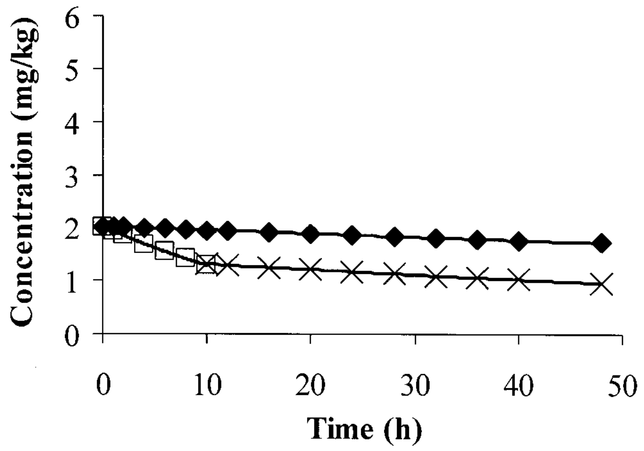


FIGURE 5 Concentration of triasulfuron on Nea Malgara soil: photodegradation under xenon arc irradiation (Suntest), first rate (□), second rate (×); reaction in the dark (◆).

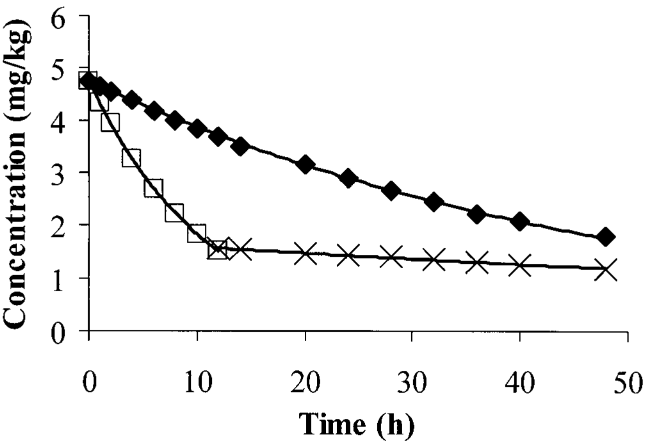


FIGURE 6 Concentration of thifensulfuron-methyl on Nea Malgara soil: photodegradation under xenon arc irradiation (Suntest), first rate (□), second rate (×); reaction in the dark (◆).

where C_t is the amount (mg) of herbicide extracted at time t per kg of soil, C_0 is the initial concentration ($\mathrm{mg\,kg^{-1}}$) of herbicide extracted at beginning of the experiment ($t = 0$), and "k" is the rate (or kinetic) constant (Figs. 2–6). The half-life time (τ) corresponds to a period of time at which the herbicide concentration is equal to half of the initial concentration (C_0), it is given by the equation $\tau = \ln 2/k$. The kinetic constants for the photodegradation reactions were calculated by subtracting the exponent "k" of the apparent degradation curves (not shown in the figures), obtained under irradiation conditions, to the exponent "k" of the degradation curves owed to hydrolysis, volatilisation, and adsorption (blank experiment carried out in the darkness). In this way, the considered "k" constants and "τ" refer to the real photochemical reaction, excluding the contribution of other factors [15]. The used procedure is valid if C_0 values of both curves are coincident.

In all performed experiments the kinetic behaviour of the photodegradation reactions were complex and characterised by a double step photoreaction. After a first period varying from 8 to 24 h the rate of reaction consistently decreases to 7–31% of the initial rate (Table II, Figs. 2–6). In this case, the photodegradation is represented by two curves with different rate constants and C_0 values. The end point of the first curve (with higher rate constant) is normally coincident with the beginning of the second curve (with lower rate constant) and represents the value of C_0 for the second curve. Thus, in a such occurrence, the herbicide photo-reaction contribution is obtained adding the quantity $(C_0–C_t)_{\mathrm{dark}}$, which disappears at the time "t" in the sample kept in the darkness, to the remaining $(C_t)_{\mathrm{light}}$ concentration detected at the same time in the irradiated sample. In this manner calculations even meet a good approximation [16].

Curves of triasulfuron photodegradation on Preveza soil under xenon are (Suntest) irradiation and in the presence of natural solar light are reported in Figs. 2 and 3, respectively. There are not significant differences between the values of kinetic parameters, but in the sunlight experiment the point of changing rate was met at 24 h with respect to the 8 h period shown in the case of xenon are irradiation (Table II). On the other hand, the reaction in the dark was more effective in the outdoor experiment giving a half-life of 26.0 h with respect to 70.7 h time calculated for the Suntest experiment. This behaviour can be due to the different environmental conditions. In the outdoor experiments soil samples, although they were protected with a quartz chamber, absorbed humidity from the atmosphere; moreover, during the hours of middle-day temperature in the quartz chamber increased up to 40°C. A more moisturised soil and higher temperatures normally favour hydrolysis reaction of herbicides, as it happens in outdoor experiment. On the contrary soil water leakage, which mostly occurs in the Suntest equipment, because of the strong ventilation rising from the air conditioner, can increase the strength of adsorption bonds; this phenomenon can rapidly reduce the free amount of the herbicide molecules available for other reaction (hydrolysis, volatilisation).

The degradation of thifensulfuron-methyl in the soil of Preveza through Suntest irradiation showed a similar behaviour (Fig. 4, Table II). The kinetic constants related to the photodegradation of thifensulfuron-methyl practically showed the same values of those obtained for triasulfuron, but with a 20 h point of changing rate. This result together with an evidenced shorter time of half-life in the dark let us suppose that thifensulfuron-methyl is not so retained as triasulfuron does on Preveza soil.

Triasulfuron and thifensulfuron-methl adsorbed on Nea Malgara soil gave the degradation trends reported in Figs. 5 and 6, respectively. Half-lives related to both the photodegradation curves and the degradation in the dark are higher than those obtained on Preveza soil (Table II). The observed behaviour can be explained considering the different amount of organic matter contained in these soils, which can be responsible of higher retention (and protection) of herbicides on Nea Malgara soil.

Generally, in soil photolysis will occur within a shallow surface zone, the depth of which depends on soil characteristics and photochemical properties of reactive substrate. Direct adbsorption of light and photolysis of organic contaminants may be influenced by adsorption reaction that is related to soil organic matter content. Indirect process could also be occurring depending on the depth and presence of sensitising substances and singlet oxygen formation [15]. Vertical depth for direct photolysis is generally restricted to 0.2–0.3 mm, indirect photolysis is to be indicating as occurring also below a layer of 0.7 mm [17]. Humic substances in soil are capable of acting as sensitisers producing reactive intermediate such as singlet oxygen, hydroxyl radicals, superoxide anion, hydrogen peroxide and peroxy radicals. Such reactive species can potentially diffuse to a depth of 1 mm depending on soil, moisture, porosity, and thermal gradient in sunlight exposed soil surface. Moreover, electronic structures, absorption spectra, and excited state lifetimes of absorbed compounds are generally different from their solution properties, making it very difficult to predict what effects may result from adsorption.

CONCLUSIONS

On the basis of the above reported data and considerations, we observed that:

1. in all performed irradiation experiments the kinetic behaviours are complex and are due to a first period, where probably a direct photolysis is prevalent on the upper layer of soil, and a second one, where soil humic substances can address an indirect photolysis;
2. in any case, photodegradation was accomplished by other reactions occurring in the soils (adsorption, hydrolysis, and volatilisation);
3. soil organic matter shows a double function, (i) adsorption site (together with other colloidal particles of soil), which can protect organic contaminants from other reactions, (ii) sensitiser for photochemical reactions;
4. the half-life times obtained by using the more organic soil from Nea Malgara were generally higher than those obtained by using the soil from Preveza;
5. despite of different light absorptions, the kinetic parameters of triasulfuron and thifensulfuron-methyl show the same values.

Acknowledgements

This work was supported by MIUR-URST (The Italian Department of Research and Education).

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