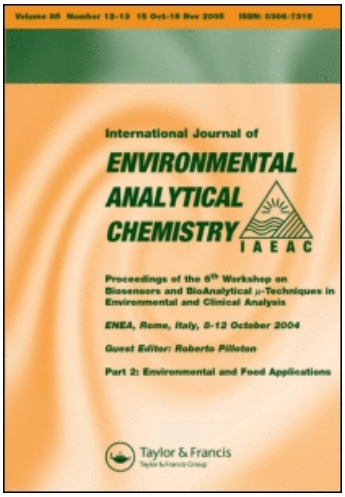

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Photochemical properties and degradation by-products of triasulphuron and thifensulphuron-methyl

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The effect of light on two sulphonylurea herbicides, triasulphuron and thifensulphuron methyl, was studied under both UV and solar simulator irradiation (Suntest). Energies of first singlet and triplet state transitions were calculated from fluorescence and phosphorescence spectra. Experiments were performed in the presence of either a singlet or a triplet quencher showing that photodegradation of both herbicides begins from a triplet state, T_1. The photolysis process of both herbicides occurred through first-order kinetics. The investigation stressed the relevance of the light exposition on the degradation rate of both herbicides. Half-lives of photolysis reactions (Suntest) in the organic solvent used in the experiments (22 and 54 h for triasulphuron and thifensulphuron methyl, respectively) are comparable with the hydrolysis rate in aqueous environment. With UV irradiation, the degradation time of both herbicides can be greatly reduced to several minutes, thus suggesting that this technique can be adopted as an efficient method of detoxification. The main photoproducts, identified by LC-ESI-MS, were: (4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea and 4-methoxy-6-methyl-1,3,5-triazin-2-amine, common to triasulphuron and thifensulphuron-methyl; 2-(2-chloroethoxy) benzenesulphonamide and (2-chloroethoxy) benzene, arising from triasulphuron degradation; 4-sulphamoyl-thiophene-3-carboxilic acid methyl ester and thiophene-3-carboxilic acid methyl ester, occurring from thifensulphuron-methyl transformation. The presence of minor by-products was also ascertained.

Keywords: Photochemistry; Triasulphuron; Thifensulphuron-methyl; Transition state; Kinetics; Photoproducts

1. Introduction

Triasulphuron and thifensulphuron-methyl are post-emergence sulphonylurea herbicides used for the treatment of different crops (wheat, barley, rye, dicotyledonous

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weeds in maize cultures, etc.), developed and well-established on the market for their low application rate and favourable environmental and toxicological properties [1–3].

The most important degradation pathways of sulphonylurea herbicides are chemical hydrolysis and microbial breakdown, and common primary degradation and metabolic reactions include the cleavage of the sulphonylurea bridge, O- and N-dealkylation, aryl and aliphatic hydroxylation, and ester hydrolysis [2]. Both triasulphuron and thifensulphuron-methyl are characterized by the presence of a triazinic ring, which can give rise to toxic metabolites through the cleavage of the sulphonylurea bridge [2]. For this reason, knowledge about the fate and behaviour of these two sulphonylurea herbicides appears to be of utmost importance for environmental protection.

The two primary hydrolytic mechanisms are acid-catalysed cleavage and base-catalysed concentration/rearrangement of the sulphonylurea linkage. This bridge is susceptible to attack by water and consequently produces the corresponding aryl sulphonamide and amino-heterocyclic portions of the molecule [2]. Since the aqueous solubility of sulphonylurea herbicides is pH-dependent, pH is expected to have a direct effect on the hydrolysis of sulphonylureas in aqueous buffer solution. Past studies have shown that triasulphuron [4, 5] and thifensulphuron-methyl [6] hydrolyse more rapidly in water at acidic pH, but remain fairly stable in neutral solutions. Alkaline hydrolysis has also been reported in the literature for both triasulphuron and thifensulphuron-methyl, although the rate constants appeared to be discordant [4, 7]. Braschi *et al*. [8] described a complete hydrolysis pathway for triasulphuron, in aqueous buffer solutions at pH values ranging from 2 to 9. The primary path of degradation was the cleavage of the sulphonylurea bridge, and a minor degradation path has also been observed such as O-demethylation and opening of the methoxy-triazine ring. The thiophene part of thifensulphuron-methyl seems to induce a particular reactivity [1, 9, 10]. The proposed acidic hydrolysis pathways for this compound in aqueous buffer solutions (pH 4 and 5) showed a concomitant cleavage of the sulphonylurea bridge and O-demethylation of the methoxy group, according to the general scheme. However, hydrolysis in alkaline conditions was found to be specific to this herbicide, leading to the saponification of the methyl ester substitute and formation of the metabolite thifensulphuron [10]. This metabolite was, however, also found to be rapidly produced in soil by biological degradation, as reported earlier by Smith *et al*. [11] and later by Brown *et al*. [12] through laboratory studies. Earlier work demonstrated the importance of microbial activities being primarily responsible for the disappearance of triasulphuron from soils particularly at lower temperatures [13, 14]. Measured half-lives in microbially active soils (pH 6.5 or 7.2) were found to be four times lower than those in sterile soils [7, 15]. In contrast, however, the microbial breakdown process appeared to be much higher in alkaline soils, although it was speculated that the type of micro-organisms present in the soil may have been the cause of a rapid disappearance of triasulphuron at high pH values [16]. Because of its thiophene moiety, thifensulphuron-methyl appears to be a compound of particular interest. Previous works have shown that the compound is degraded microbially [11, 17], and the initial degradation product in soil has been identified as herbicidally inactive thifensulphuron acid [12, 18]. Steric and electronic features of thifensulphuron-methyl that may account for its rapid deesterification in soil and water have been described [19]. Comparison of degradation curves in sterile and non-sterile soils [7, 18] suggested a first microbial deesterification step followed by chemical processes as described later in hydrolysis kinetics under aqueous buffer solutions [10].

The photochemical degradation of triasulphuron in aqueous solution has also been reported [20]. Irradiation at 254, 300, and 360 nm led to pseudo-first-order degradation of the herbicide, producing several metabolites such as (2-chloroethoxy) benzene and (4-methoxy-6-methyl-1,3,5-triazin-2-yl) urea. Unfortunately, with an aqueous solution, photochemical reactions could not be distinguished from hydrolysis. As cited above, the thiophene part of thifensulphuron-methyl can induce a particular reactivity, but no further information is available on its photochemical reactivity. Besides, we believe that a photochemical investigation can be of great importance in the case of post-emergence herbicides because they are usually sprayed on soil surfaces and plant leaves, and could undergo natural photodegradation, especially in sunny areas. Moreover, UV photodegradation could be a useful method of detoxification of collected waste waters [3].

In the case of rimsulphuron, another sulphonylurea herbicide, the photolytic process under simulated sunlight was as important as the hydrolytic effect [3]. Notably, the photolysis rate increased with acidity, whereas hydrolysis rate decreased with a slope closer to the hydrolysis curve but having an opposite sign, the crossing point indicating that at pH 7.3 (a diffuse pH value both in biotic and abiotic environments) the two reactions occur at the same rate. The sunlight effect at pH 9 was not completely negligible with respect to the hydrolysis reaction, while the photolysis contributions at pH 7 and pH 5 were higher than the hydrolysis efficiency at the same pH values.

This article deals with photochemical properties and transformation pathways of triasulphuron and thifensulphuron-methyl under light irradiation using anhydrous acetonitrile, as a suitable solvent to avoid hydrolysis reactions. Relevant questions about these two sulphonylureas are: (1) Can solar light have some degradation effect? (2) Can UV irradiation be an effective method to eliminate their residues from constrained environments?

2. Experimental

2.1 *Chemicals*

Triasulphuron [21] (purity 98.7%; MW 401.8; vapour pressure 100 fPa at 20°C; water solubility 815 mg L^{-1} at pH 7–25°C; pK_a 4.64 at 20°C; $C\log P = 2.19$ at pH 5–25°C), 1-[2-(2-chloroethoxy)-phenylsulphonyl]-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl) urea (CAS RN 82097-50-5) (figure 1), and thifensulphuron-methyl [21] (purity 98.8%; MW 387.4; vapour pressure 17 nPa at 25°C; water solubility 6270 mg L^{-1} at pH 7–25°C; pK_a 4.0 at 25°C; $C\log P = 1.69$ at pH 5–25°C), methyl 3-[3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl) ureidosulphonyl] thiophene-2-carboxylate (CAS RN 79277-27-3) (figure 1) were purchased from Dr Ehrenstorfer GmbH (Augsburg, Germany). All solvents (pesticide grade), reagents (analytical grade) and filters (disposable sterilized packet) were purchased from Sigma-Aldrich (St. Louis, MO), and Fluka Chemie (Buchs, Switzerland). Ultrapure water was obtained by means of a Millipore (Billerica, MA) Milli-Q system.

2.2 *Preparation of samples*

All glass apparatus were heat-sterilized by autoclaving for 60 min at 121°C before use. Aseptic handling materials and laboratory facilities were used throughout the study to

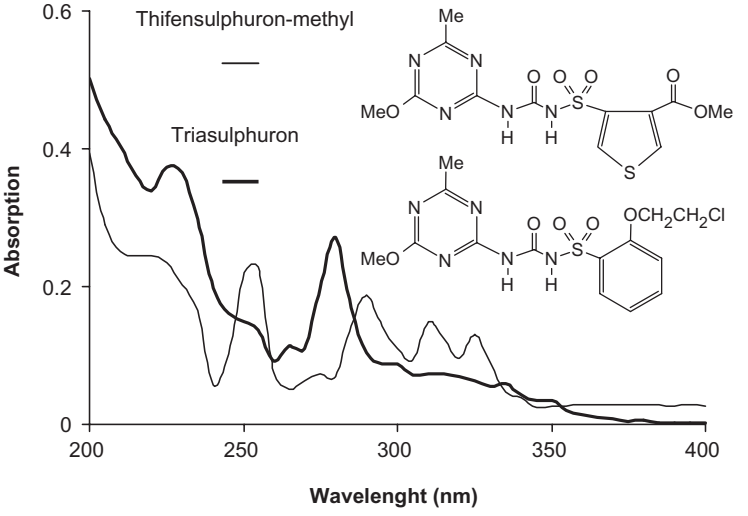

Figure 1. Chemical structures and UV absorptions of triasulphuron and thifensulphuron-methyl (at 5 nm bandwidth).

maintain sterility. A stock solution (~1 mM) of each active ingredient (AI) in anhydrous acetonitrile was prepared and kept in the dark at 4°C. Calibration and test solutions of each AI were prepared when used by dilution from stock solutions. We chose acetonitrile because this solvent is suitable for understanding photochemical and spectroscopic behaviour of organic compounds [22] and to prevent as much as possible any undesirable hydrolysis reactions. Moreover, we speculate that the knowledge of photochemical properties in the organic solvent can be useful because, with post-emergence treatments, a large amount of AI remains on the exposed site of leaves and may interact with the waxy and fatty substances, which cover the surface of leaves [3].

2.3 *Equipment*

UV spectra of sulphonylureas in acetonitrile (0.1 mM) were recorded on a Cary 2300 spectrophotometer (Varian, Harbor City, CA), as reported in figure 1. Fluorescence and phosphorescence spectra were obtained in the same solvent with a Jobin Yvon 3D spectrofluorimeter. Fluorescence spectra were recorded using diphenylanthracene (DPA) as actinometer. Phosphorescence spectra were recorded under liquid nitrogen in the diethyl ether/2-methylbutane/ethanol (5/5/2) mixture (EPA), using acetophenone as actinometer.

Photochemical reactions were performed using a solar simulator (Suntest CPS+, Heraeus Industrietechnik GmbH, Hanau, Germany), equipped with a xenon lamp (1.1 kW) that was protected with a quartz plate. The irradiation chamber was maintained at 25°C by both circulating water from a thermostatic bath and a conditioned airflow. To facilitate comparisons between the two herbicides, the initial concentration of test solutions was settled at 0.1 mM for both (40.18 and 38.74 mg L^{-1} for triasulphuron and thifensulphuron-methyl, respectively). Solutions at the same concentrations used for the Suntest experiments were irradiated in a Pyrex reactor (250 mL) at 20°C (water circulation temperature controlled), using a Philips HPK 125W UV-Hg

high-pressure lamp (Philips, Eindhoven, The Netherlands) covered with a borosilicate protection.

2.4 *Actinometry*

Actinometric measurements were performed by using the uranyl oxalate photo-reaction to test the mercury arc efficiency at the beginning and end of the experiment, and to evaluate the quantum yield of pesticide photo-reactions [22]. In the last case, to prevent the shield effect due to the formation of an appreciable quantity of by-products, the reactions were stopped after 5 min of irradiation. At the end of each irradiation experiment, the efficiency of Hg-UV arc was not appreciably diminished from the reference value of 1.97×10^{16} photons $cm^{-1} s^{-1}$. Quantum yields were also measured under xenon light; in this case, reactions were stopped after 15 min of irradiation. The measured irradiance of the xenon arc in the range 280–800 nm was practically constant (632 W m^{-2}) during the entire duration of the irradiation tests.

2.5 *Analytical instrumentation*

An HP 1090 (Hewlett Packard, Palo Alto, CA) liquid chromatograph equipped with a diode array detector, C_{18} Dionex (Sunnyvale, CA) Omnipac PCX-500 (5 μm) packed column (250 × 4.6 mm) plus guard column was used at a flow rate of 1 mL min^{-1}. An acetonitrile–water mixture 1 : 1 (v : v) (pH = 2.75, acetic acid) was adopted as mobile phase for triasulphuron; the detection wavelength was selected at 230 nm. A volumetric mixture from 10 to 40% of acetonitrile in water (pH 3, acetic acid) was used as mobile phase for thifensulphuron-methyl; the detection wavelength was tuned at 254 nm. According to literature criteria [3, 23, 24], metabolites were also qualitatively determined and confirmed by LC-ESI-MS analysis using an LCQ Classic ion-trap mass spectrometer (Thermo-Finnigann, San Jose, CA) equipped with a Spectra System P4000 pump. The column was a Supelcosil LC-ABZ, C_{18} (5 μm, 250 × 4 mm) with a guard column of the same material (Supelco Inc., Bellefonte, PA), and the mobile phases consisted of 0.1% formic acid in water (solvent A) and methanol (solvent B). The following gradient was applied: 30–43% B in 0–8 min; 43–60% B in 8–20 min; and 60% B in 20–24 min. At the end of the gradient, a re-equilibration phase of 6 min was allowed between samples. The flow rate was 0.8 mL min^{-1}, which was reduced to 200 μm min^{-1}, a 3 : 1 split system behind the column, at the entrance of the electrospray source. Positive-ion electrospray ionization (ESI) mass spectrometry was used for the detection and quantification of metabolites. The voltage on the ESI needle was set at 5 kV, producing a spray current of approximately 80 μA. The capillary voltage was set at 14 V, and the temperature of the heated capillary was 200°C. The sheath gas flow rate used was 60 (arbitrary units), and the auxiliary gas was set to zero.

2.6 *Procedures*

Samples were irradiated, and the disappearance of the herbicides at various illumination times was determined by liquid chromatography. Control samples (having the same initial concentration of irradiated samples) were kept in the dark at the same temperature, and the herbicides were detected at the same times of irradiated samples to measure the disappearance due to hydrolysis or to confirm that the degradation

process would only be the result of photochemical reactions. Three replicates were carried out for each experiment. The calibration plots were performed in the concentration range 2.0×10^{-4} to $0.1\,\text{mmol}\,\text{L}^{-1}$ for triasulphuron, giving a linear response with $r > 0.99967$, and in the range 5.0×10^{-4} to $0.1\,\text{mmol}\,\text{L}^{-1}$ for thifensulphuron-methyl, $r > 0.99978$. At a signal-to-noise ratio of 3, the limits of quantitation in the acetonitrile standard solution were 1.0×10^{-4} and $3.5 \times 10^{-4}\,\text{mmol}\,\text{L}^{-1}$ for triasulphuron and thifensulphuron-methyl, respectively.

2.7 *Quenching experiments*

To better understand the photochemical degradation mechanism of the two sulphonylureas, additional experiments were performed under the Suntest irradiation system. We wished to clarify whether the photochemical reaction occurred through the first excited singlet state or the first excited triplet state.

Under the aforementioned environmental conditions and herbicide concentrations, the reactions were repeated adding (at $t = 0$) to the acetonitrile solution of each AI either a singlet [naphthalene ($E_S = 385\,\text{kJ}\,\text{mol}^{-1}$, $E_T = 253\,\text{kJ}\,\text{mol}^{-1}$)] or a triplet quencher [pyrene ($E_T = 203\,\text{kJ}\,\text{mol}^{-1}$, $E_S = 322\,\text{kJ}\,\text{mol}^{-1}$)], and kinetics were recalculated. Either under light irradiation or in the dark, a molar ratio of 1/10 herbicide/quencher was used [22, 25].

3. Results and discussion

3.1 *Photochemical properties*

The UV spectrum of triasulphuron (figure 1) showed absorption maxima at $\lambda_1 = 224\,\text{nm}$ ($\log \varepsilon_1 = 4.48$) and $\lambda_2 = 280\,\text{nm}$ ($\log \varepsilon_2 = 4.39$). The UV spectrum of thifensulphuron-methyl showed absorption maxima at $\lambda_1 = 254\,\text{nm}$ ($\log \varepsilon_1 = 4.31$), $\lambda_2 = 288\,\text{nm}$ ($\log \varepsilon_2 = 4.11$), $\lambda_3 = 312\,\text{nm}$ ($\log \varepsilon_3 = 3.82$), and $\lambda_4 = 326\,\text{nm}$ ($\log \varepsilon_4 = 3.73$). Recorded absorptions of herbicides are consistent with the emissions of both the xenon-Suntest system (total passing wavelength: $280\,\text{nm} < \lambda < 800\,\text{nm}$) and Hg-UV reactor (total passing wavelength: $300\,\text{nm} < \lambda < 580\,\text{nm}$). Absorptions of thifensulphuron-methyl are better covered by light emissions. Fluorescence and phosphorescence were recorded using the excitation wavelengths $\lambda\text{tria} = 280\,\text{nm}$ and $\lambda\text{thife} = 288\,\text{nm}$, obtaining emission bands centred at $\lambda\text{tria}_{\text{flu}} = 300\,\text{nm}$, $\lambda\text{thife}_{\text{flu}} = 312\,\text{nm}$, $\lambda\text{tria}_{\text{pho}} = 410\,\text{nm}$, and $\lambda\text{thife}_{\text{pho}} = 412\,\text{nm}$. From fluorescence and phosphorescence spectra, it was possible to calculate the energies of first singlet and triplet state transitions [22, 25], as reported in table 1 for both the herbicides. All transition energies are compatible with light energies emitted from both the xenon and mercury arcs (data not shown).

3.2 *Quenching effect*

Neither naphthalene nor pyrene affected the concentration of the herbicides in the dark, whereas the presence of the singlet quencher considerably inhibited the photo-reaction of both herbicides, as did the triplet quencher (tables 1 and 2). This behaviour suggests a mechanism involving the first excited triplet state and a rapid evolution of the photolysis reaction [22, 25, 26].

Table 1. Energies of first transition states of triasulphuron and thifensulphuron-methyl and selected quenchers.

Herbicide or quencher	Transition state	Energy ($kJ\,mol^{-1}$)	Degradation inhibited by naphthalene	Degradation inhibited by pyrene	Mechanism through
Triasulphuron	S_1	405.5	Yes	–	S_1 or T_1
	T_1	215.48	–	Yes	T_1
Thifensulphuron-methyl	S_1	401.4	Yes	–	S_1 or T_1
	T_1	217.86	–	Yes	T_1
Naphthalene [22]	S_1	385			
	T_1	253			
Pyrene [22]	S_1	322			
	T_1	203			

Table 2. Kinetic parameters of triasulphuron and thifensulphuron-methyl photodegradation: reaction order (n), determination coefficient (r^2), half-life ($t_{0.5}$), kinetic constant (k), quantum yield (Φ).[a]

Herbicide	Light source	n	r^2	$t_{0.5}$ (min)	k (per min)	Φ
			Absence of quenchers			
Triasulphuron	Suntest	1	0.964	1338	5.18×10^{-4}	1.38×10^{-5}
	Hg-UV	1	0.970	1.7	4.07×10^{-1}	9.21×10^{-2}
Thifensulphuron-methyl	Suntest	1	0.965	3240	2.14×10^{-4}	4.04×10^{-6}
	Hg-UV	1	0.966	16.2	4.28×10^{-2}	6.41×10^{-4}
			Presence of naphthalene			
Triasulphuron	Suntest	1	0.984	4636	1.49×10^{-4}	–
Thifensulphuron-methyl	Suntest	1	0.978	8222	8.43×10^{-5}	–
			Presence of pyrene			–
Triasulphuron	Suntest	1	0.981	3988	1.74×10^{-4}	–
Thifensulphuron-methyl	Suntest	1	0.987	7402	9.36×10^{-5}	–

[a]Values were obtained on the basis of three replicate experiments. Initial concentrations $C_0 = 0.1\,mmol\,L^{-1}$.

3.3 *Photodegradation*

Table 2 shows quantum yields (Φ) and kinetic parameters of the photochemical reactions, calculated considering three replicates for each experiment. In all cases considered in our experiments, photo-reactions of the first order resulted, and the half-life of triasulphuron was always lower than thifensulphuron-methyl. The pure standard solutions used as a control in the darkness did not show any significant degradation during the experiment.

Figure 2 shows the fraction $[1 - (C_0 - C_t)/C_0]$ of (a) triasulphuron and (b) thifensulphuron-methyl remaining in the acetonitrile solution under Suntest irradiation and in the dark. Figure 3 shows the fraction of (a) triasulphuron and (b) thifensulphuron-methyl remaining under Hg-UV irradiation. $(C_0 - C_t)/C_0$ is the fraction that disappeared at time t. Triasulphuron was rapidly degraded under Hg-UV irradiation, with a half-life of 1.7 min, which is close to the value of 2.0 min found by Pusino *et al.* [20] under 254 nm UV irradiation, and calculated through half-order kinetics by Vulliet *et al.* [27] in an experiment of photodegradation performed on titanium dioxide ($t_{0.5} = 1.2$ min). Photo-degradation of thifensulphuron-methyl was much faster under Hg-UV than under Suntest irradiation. The UV half-life of 16.2 min was in agreement with the value of 9.5 min calculated by Maurino *et al.* [28] for the same herbicide and obtained using TiO_2 as a reaction activator.

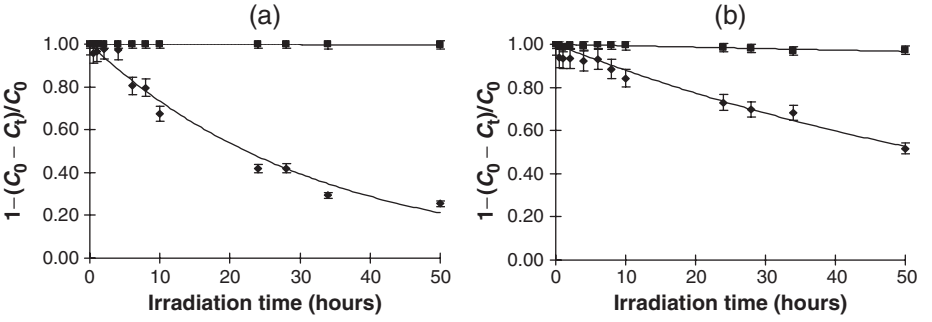

Figure 2. Fraction of (a) triasulphuron and (b) thifensulphuron-methyl remaining after Suntest irradiation (♦), and in the dark (■). Error bars represent the standard deviations of three replicate samples.

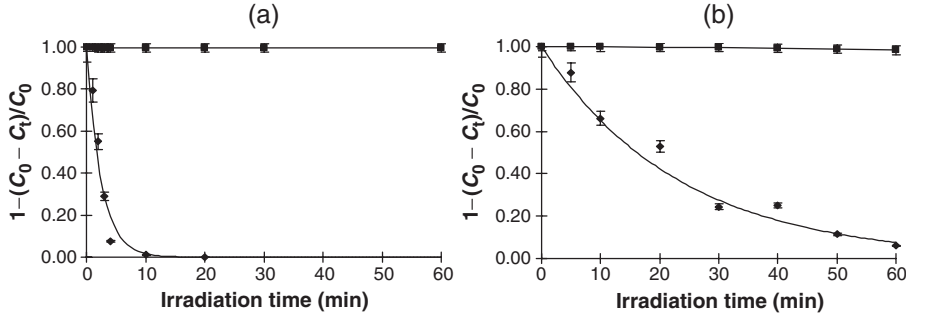

Figure 3. Fraction of (a) triasulphuron and (b) thifensulphuron-methyl remaining after Hg-UV irradiation (♦) and in the dark (■). Error bars represent the standard deviations of three replicate samples.

3.4 *Photoproducts*

The main metabolites identified in the acetonitrile solutions during the first 10 h of Suntest irradiation were: (4-methoxy-6-methyl-1,3,5-triazin-2-yl) urea (**3**), common to triasulphuron and thifensulphuron-methyl, and 2-(2-chloroethoxy) benzenesulphonamide (**7**), arising from triasulphuron degradation, and 4-sulphamoyl-thiophene-3-carboxilic acid methyl ester (**4**), occurring from thifensulphuron-methyl (table 3). After 10 h of irradiation, the formation of 4-methoxy-6-methyl-1,3,5-triazin-2-amine (**2**) (from triasulphuron and thifensulphuron-methyl), (2-chloroethoxy)benzene (**8**) (from triasulphuron), thiophene-3-carboxylic acid methyl ester (**5**) (from thifensulphuron-methyl), and a multitude of small by-products, which could not be identified with simple analytical methods, were also observed (table 3 and figure 4). In some samples collected after 34 h of irradiation, it was also possible to identify the acid forms of compounds '**4**' and '**5**' (table 3), arising from an O-demethylation of the methoxy group.

Metabolites '**2**', '**3**', '**7**' and '**8**' were previously identified as triasulphuron derivatives in photodegradation experiments performed by Pusino *et al.* [20]. Compounds '**2**' and '**7**' were also found by Braschi *et al.* [8] from hydrolysis of the same AI. Compound '**2**' was also identified during hydrolysis and biotransformation of metsulphuron-methyl [29]. Cambon *et al.* [30], and Cambon and Baside [10] showed the formation of metabolite '**4**' from hydrolysis and soil biotransformation of thifensulphuron-methyl. The saponification of the methyl ester substitute in thifensulphuron-methyl and its

Table 3. LC-MS retention times (R_t) and mass spectral characteristics (m/z) of parent molecules and their degradation products.

Compound	Chemical name	R_t (min)	MS fragment ions m/z (abundance%)
1	Thifensulphuron-methyl	8.23	388 (100, $[M+H]^+$), 270 (10), 205 (10), 167 (90), 141 (30)
2	4-Methoxy-6-methyl-1,3,5,-triazin-2-amine	4.70–4.76	141 (100, $[M+H]^+$), 125 (20)
3	(4-Methoxy-6-methyl-1,3,5-triazin-2-yl) urea	5.74–5.80	184 (100, $[M+H]^+$), 167 (60), 141 (40)
4	4-Sulphamoyl-thiophene-3-carboxilic acid methyl ester	7.15	221 (60, $[M+H]^+$), 147 (100), 129 (40)
5	Thiophene-3-carboxylic acid methyl ester	10.33	143 (100, $[M+H]^+$), 115 (30)
6	Triasulphuron	10.02	402 (100, $[M+H]^+$), 300 (20), 167 (70), 141 (10)
7	2-(2-Chloro-ethoxy) benzene sulphonamide	8.13	236 (100, $[M+H]^+$), 186 (30), 81 (10)
8	(2-Chloro-ethoxy) benzene	11.68	157 (100, $[M+H]^+$), 107 (20), 81 (10)

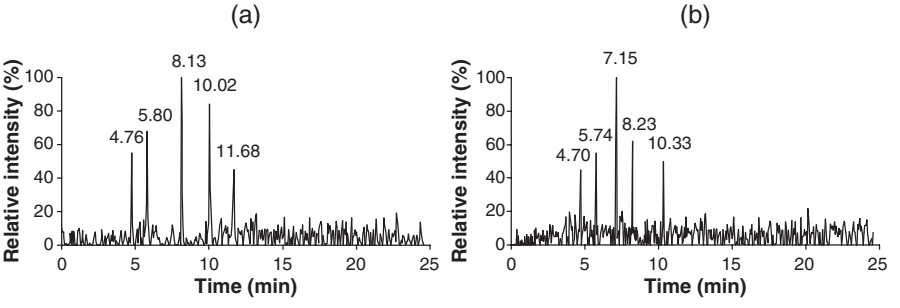

Figure 4. Reconstructed LC-ESI-MS chromatograms of parent molecules and Suntest degradation products obtained injecting the 24 h irradiated sample for (a) triasulphuron and 34 h for (b) thifensulphuron-methyl.

derivatives was also found by Cambon and Bastide [10] and Brown *et al*. [12] as a result of the hydrolysis reaction in water and soil.

Figure 5 shows the evolution of identified photoproducts (table 3) during Suntest irradiation of herbicides. Peak areas of metabolites '**2**' and '**8**', coming from triasulphuron transformation, increased during the entire duration of the experiment. Whereas the amounts of products '**3**' and '**7**' increased during the first 10 h of irradiation, they were rapidly diminishing thereafter (figure 5a). The observed behaviour suggests that the photodegradation of triasulphuron follows two pathway (figure 6a): (1) cleavage of the S–N and S–C bonds in the sulphonyl-urea bridge, which gives rise to compounds '**3**' and '**8**', and subsequent transformation of the triazinyl-urea moiety (**3**) into the trianzin-amine derivative (**2**); (2) cleavage of C–N bonds in the urea linkage, building up metabolites '**2**' and '**7**', followed by the conversion of *R*-benzenesulphonamide (**7**) into *R*-benzene (**8**).

A similar pathway can be proposed for thifensulphuron-methyl. Trends of derivatives '**2**' and '**5**' in figure 5(b) were continuously growing, and metabolites '**3**' and '**4**' were falling after the first 10 h of irradiation. Also in this case, we can presume the coexistence of more reactions (figure 6b): (i) cleavage of the S–N and S–C bonds

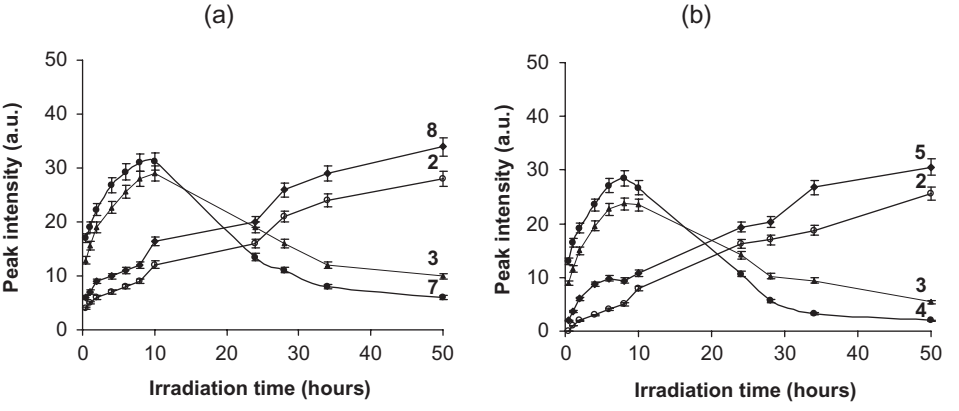

Figure 5. Evolution of photoproducts (table 3) during Suntest irradiation of (a) triasulphuron and (b) thifensulphuron-methyl. Error bars represent the standard deviations of three replicate samples.

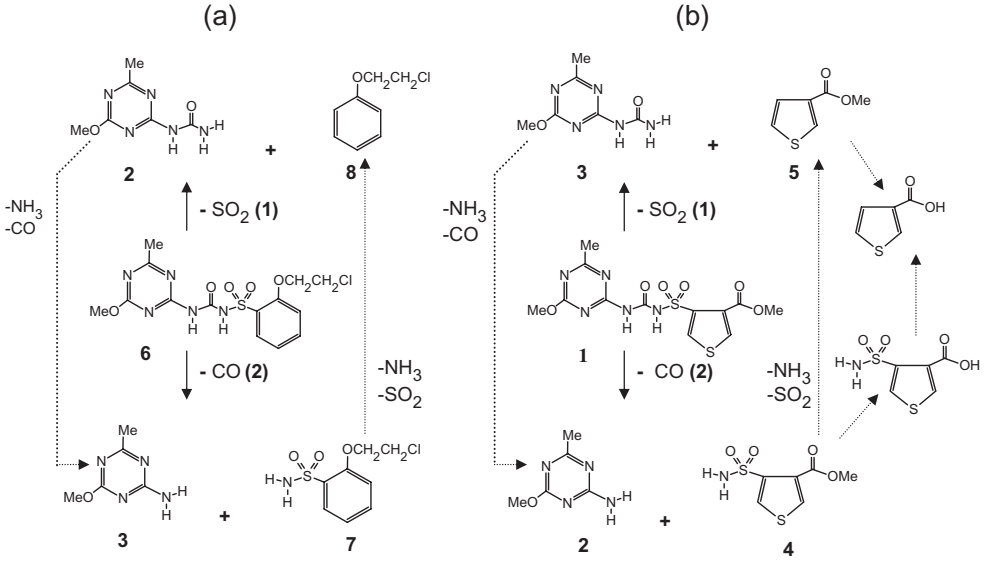

Figure 6. Proposed photodegradation pathway for (a) triasulphuron and (b) thifensulphuron-methyl on the basis of metabolites identified under Suntest irradiation.

(compounds '**3**' and '**5**'), and conversion of metabolite '**3**' into the derivative '**2**'; (ii) cleavage of carbonyl C–N bonds (compounds '**2**' and '**4**'), and loss of sulphamoyl moiety of compound '**4**' giving rise to derivative '**5**'. Moreover, the methyl esters '**4**' and '**5**' can be transformed into the corresponding carboxylic acids.

To provide further evidence of the suggested reactions, a separate experiment was performed on both herbicides, collecting the gaseous phase developed on the bottom of the photo-reactor in the Suntest chamber for another 50 h by means of a membrane dry pump (data not shown). The gas-chromatographic analysis showed the relevant presence of CO, NH_3, and SO_2 in the gaseous mixture, confirming the acceptability of the proposed pathway.

4. Conclusion

The investigation stressed the importance of light exposure on the degradation rate of both herbicides. The half-lives of photolysis reactions in the organic solvent used in the experiments (22 and 54 h for triasulphuron and thifensulphuron-methyl, respectively) are comparable with the hydrolysis rate in the aqueous environment. This probably means that the photolysis of these herbicides can be a very important process in organic environments, and degradation on the surfaces of leaves is also possible, particularly in sunny areas and seasons. UV irradiation allows the degradation time of both herbicides to be reduced considerably, thus suggesting that this technique can be adopted as an efficient method of detoxification.

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